

Docket No. : ASMJP.055DV1  
Application No. : 10/759,953  
Filing Date : January 16, 2004

---

Customer No.: 20,995

## **APPENDIX B**

### **EVIDENCE APPENDIX**

Appendix B includes the following documents:

Shang (U.S. Pat. No. 5,788,778),

U.S. Pat. No. 6,274,058,

Sun (U.S. Pat. Pub. No. 2002/0033183),

Yin et al., (PCT Pub. No. WO 99/20812),

Fukuda (U.S. Pat. Pub. No. 2005/0139578),

Shang (EP 0697467))

Signed declaration, submitted to the Examiner in the Response dated January 12, 2007.



US005788778A

**United States Patent** [19]

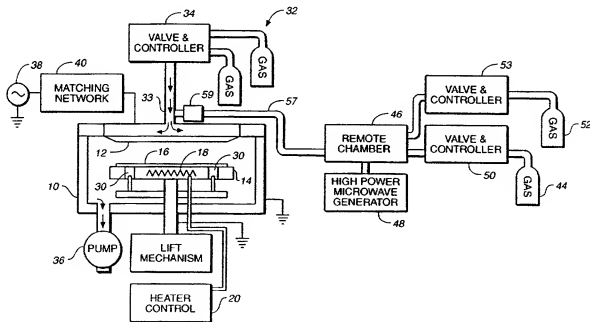
Shang et al.

[11] **Patent Number:** 5,788,778[45] **Date of Patent:** Aug. 4, 1998[54] **DEPOSITION CHAMBER CLEANING  
TECHNIQUE USING A HIGH POWER  
REMOTE EXCITATION SOURCE**[75] **Inventors:** Quanyuan Shang, San Jose; Kam S.  
Law, Union City; Dan Maydan, Los  
Altos Hills, all of Calif.[73] **Assignee:** Applied Komatsu Technology, Inc.,  
Tokyo, Japan[21] **Appl. No.:** 707,491[22] **Filed:** Sep. 16, 1996[51] **Int. Cl.<sup>6</sup>** ..... B08B 7/04; B08B 5/00;  
C03C 23/06; C03C 15/00[52] **U.S. Cl.** ..... 134/1; 134/2; 134/31;  
134/37; 134/21; 156/345; 156/643.1; 156/646.1;  
156/657.1[58] **Field of Search** ..... 134/1, 2, 3, 11,  
134/30, 902, 37; 156/643.1, 646.1, 656.1,  
657.1, 345[56] **References Cited**

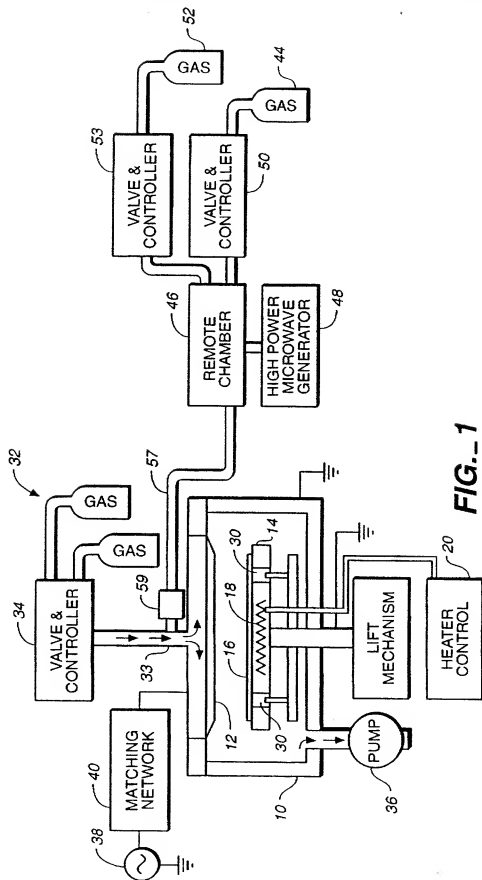
## FOREIGN PATENT DOCUMENTS

0697467 2/1996 European Pat. Off.  
4132559 4/1993 Germany  
WO 96/15545 5/1996 WIPO*Primary Examiner*—Ponnathapura Achutamurthy  
*Assistant Examiner*—Padmashri Ponnaluri  
*Attorney, Agent, or Firm*—Fish & Richardson P.C.[57] **ABSTRACT**

A method for cleaning a deposition chamber that is used in fabricating electronic devices including the steps of delivering a precursor gas into a remote chamber that is outside of the deposition chamber, activating the precursor gas in the remote chamber via a high power source to form a reactive species, flowing the reactive species from the remote chamber into the deposition chamber, and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

**21 Claims, 2 Drawing Sheets****APPENDIX B**

Appl. No.: 10/759,953



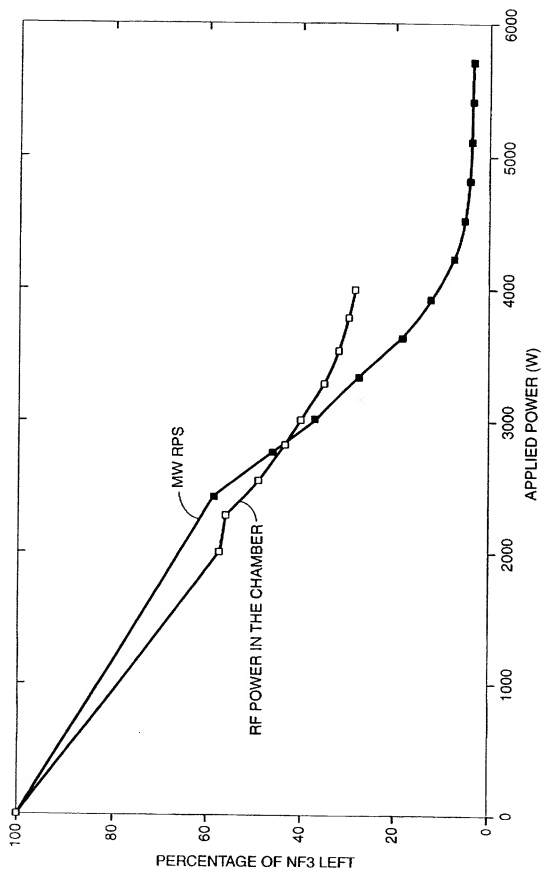


FIG.-2

# DEPOSITION CHAMBER CLEANING TECHNIQUE USING A HIGH POWER REMOTE EXCITATION SOURCE

## BACKGROUND OF THE INVENTION

Plasma assisted chemical reactions have been widely used in the semiconductor and flat panel display industries. One example is plasma-enhanced chemical vapor deposition (PECVD), which is a process that is used in the manufacture of thin film transistors (TFT) for active-matrix liquid crystal displays (AMLCDs). In accordance with PECVD, a substrate is placed in a vacuum deposition chamber that is equipped with a pair of parallel plate electrodes. One of the electrodes, e.g. the lower electrode, generally referred to as a susceptor, holds the substrate. The other electrode, i.e., the upper electrode, functions as a gas inlet manifold or shower head. During deposition, a reactant gas flow into the chamber through the upper electrode and a radio frequency (RF) voltage is applied between the electrodes to produce a plasma within the reactant gas. The plasma causes the reactant gas to decompose and deposit a layer of material onto the surface of the substrate.

Though such systems are designed to preferentially deposit the material onto the surface of the substrate, they also deposit some material onto other interior surfaces within the chamber. Consequently, after repeated use, these systems must be cleaned to remove the deposited layer of material that has built up in the chamber. To clean the chamber and the exposed components within the chamber, an in-situ dry cleaning process is commonly used. According to the in-situ technique, precursor gases are supplied to the chamber. Then, by locally applying a glow discharge plasma to the precursor gases within the chamber, reactive species are generated. The reactive species clean the chamber surfaces by forming volatile compounds with the process deposit on those surfaces.

This in-situ cleaning technique has several disadvantages. First, it is inefficient to use a plasma within the chamber to generate the reactive species. Thus, it is necessary to use relatively high powers to achieve an acceptable cleaning rate. The high power levels, however, tend to produce damage to the hardware inside of the chamber thereby significantly shortening its useful life. Since the replacement of the damaged hardware can be quite costly, this can significantly increase the per substrate cost of product that is processed using the deposition system. In the current, highly competitive semiconductor fabrication industry where per substrate costs are critical to the cost conscious purchasers, the increased operating costs resulting from having to periodically replace parts that are damaged during the cleaning process is very undesirable.

Another problem with the conventional in-situ dry cleaning processes is that the high power levels required to achieve acceptable cleaning rates also tend to generate residues or byproducts that can damage other system components or which cannot be removed except by physically wiping off the internal surfaces of the chamber. As an example, in a deposition system in which the chamber or the process kit components (e.g. heater, shower head, clamping rings, etc.) are made of aluminum, an  $\text{NF}_3$  plasma is often used to clean the interior surfaces. During the cleaning process, a certain amount of  $\text{AlF}_3$  is formed. The amount that is formed is greatly increased by the ion bombardment that results from the high plasma energy levels. Thus, a considerable amount of  $\text{AlF}_3$  can be formed in the system. Unfortunately, this material cannot be etched away by any

known chemical process, so it must be removed by physically wiping the surfaces.

One solution is to excite the plasma in a remote chamber. In this method, a remote excitation source is used outside of the process chamber to generate a reactive species. This species is supplied to the process chamber to assist in carrying out a particular process, e.g. dry cleaning the chamber.

This method has several drawbacks. First, the value of the applied plasma power used in such systems (typically 500-1500 watts) does not achieve complete breakdown of the feed gas, typically  $\text{NF}_3$ . The feed gas which is not broken down by the plasma may have adverse environmental impacts when the same is pumped out of the system. Purchasers often prefer products whose impact on the environment is either negligible or helpful.

Second, the value of the applied pressure used in such systems is generally low. The effect of this is that the plasma is less localized. An undesirable result of the lack of localization is that certain components in and near the remote excitation chamber may become burned by the hot plasma. For example, this may occur near the neck of the tube connecting the remote chamber to the deposition chamber, particularly on the side of the tube near the remote chamber.

Third, the initiation of a plasma with a microwave energy having the value of power used in such systems (typically 500-1500 watts) typically requires a complicated automatic tuning procedure because such plasmas are not stable otherwise. That is, such plasmas will extinguish without automatic tuning.

## SUMMARY OF THE INVENTION

In one aspect, the invention concerns a method for cleaning a deposition chamber that is used in fabricating electronic devices. Steps in the method include delivering a precursor gas into a remote chamber that is outside of the deposition chamber and activating the precursor gas in the remote chamber to form a reactive species using a power of from about 3,000 Watts to about 12,000 Watts. Other steps include flowing the reactive species from the remote chamber into the deposition chamber and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

Implementations of the method include the following. The step of activating the precursor gas is performed by using a remote activation source. The precursor gas is selected from the group of gases consisting of all halogens and gaseous compounds thereof, and may be selected from the group of gases consisting of chlorine, fluorine, and gaseous compounds thereof. The remote activation source is a microwave energy source. The method may further include flowing a carrier gas into the remote activation chamber, where the carrier gas is selected from the group of gases consisting of nitrogen, argon, helium, hydrogen, and oxygen.

In another aspect, the invention is directed to a method of cleaning a process chamber. Steps of the method include delivering a precursor gas into a remote chamber that is outside of the process chamber so that there is a pressure differential between the remote chamber and the process chamber and activating the precursor gas in the remote chamber to form a reactive species using a power of from about 3,000 Watts to about 12,000 Watts. Other steps include flowing the reactive species from the remote chamber into the process chamber.

Implementations of the invention include the following. A step may be included of using a local activation source to further excite the reactive species that has been flowed into the process chamber from the remote chamber, and using the reactive species that has been further excited by the local activation source to perform the cleaning process in the process chamber. The pressure differential is at least about 4.5 Torr, and the pressure in the remote chamber is at least about 15 Torr.

In another aspect, the invention is directed to a deposition apparatus that can be connected to a source of precursor gas for cleaning. The apparatus includes a deposition chamber, a remote chamber that is outside of the deposition chamber, an high power activation source adapted to deliver energy of a high power into the remote chamber, a first conduit for flowing a precursor gas from a remote gas supply into the remote chamber where it is activated by the activation source to form a reactive species, and a second conduit for flowing the reactive species from the remote chamber into the deposition chamber.

Implementations of the invention include the following. The apparatus may include a valve and flow control mechanism which controls the flow of precursor gas into the remote chamber, and a valve and flow control mechanism which controls the flow of a carrier gas that is different from the precursor gas into the remote chamber.

In a further aspect, the invention is directed to a method for cleaning a deposition chamber that is used in fabricating electronic devices. Steps of the method include delivering a precursor gas into a remote chamber that is outside of the deposition chamber and activating the precursor gas in the remote chamber to form a reactive species using a power of from about 12,000 Watts per liter to about 48,000 Watts per liter of remote chamber volume. Other steps include flowing the reactive species from the remote chamber into the deposition chamber and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

In a further aspect, the invention is directed to a method for cleaning a deposition chamber that is used in fabricating electronic devices. The method includes steps of delivering a precursor gas into a remote chamber that is outside of the deposition chamber and activating the precursor gas in the remote chamber to form a reactive species using a power of from about 3,000 Watts to about 12,000 Watts using a fixed tuning high power plasma source. Other steps include flowing the reactive species from the remote chamber into the deposition chamber, and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a block diagram of a high power PECVD system which embodies the invention.

FIG. 2 shows a graph of a percentage amount of cleaning gas breakdown versus applied power.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the described embodiment, we used a model AKT-1600 PECVD System manufactured by Applied Komatsu Technology, modified as described herein. The AKT-1600 PECVD is designed for use in the production of active-matrix liquid crystal displays (AMLCDs). It is a modular system with multiple process chambers which can be used

for depositing amorphous silicon, silicon nitride, silicon oxide and oxynitride films. The invention, however, may be used with any commercially available deposition system.

Referring to FIG. 1, the PECVD system modified in accordance with invention includes a deposition chamber 10 inside of which is a gas inlet manifold (or shower head) 12 for introducing deposition gases and a susceptor 14 for holding a substrate 16 onto which material is to be deposited. Inlet manifold 12 and susceptor 14, which are both in the form of parallel plates, also function as upper and lower electrodes, respectively. The lower electrode and the chamber body are connected to ground. An RF generator 38 supplies RF power to the upper electrode through a matching network 40. RF generator 38 is used to generate a plasma between the upper and lower electrodes.

Susceptor 14 includes a resistive heater 18 for heating the substrate during deposition. An external heater control module 20 powers the heaters to achieve and maintain the susceptor at an appropriate temperature level as dictated by the process being run in the system.

Outside of chamber 10, there is a gas supply 32 containing the gases that are used during deposition. The particular gases that are used depend upon the materials are to be deposited onto the substrate. The process gases flow through an inlet port into the gas manifold and then into the chamber through the shower head. An electronically operated valve and flow control mechanism 34 controls the flow of gases from the gas supply into the chamber. Also connected to the chamber through an outlet port is a vacuum pump 36, which is used to evacuate the chamber.

In accordance with the invention, a second gas supply system is also connected to the chamber through inlet port 33. The second gas supply system supplies gas that is used to clean the inside of the chamber after a sequence of deposition runs. By cleaning, we mean removing deposited material from the interior surfaces of the chamber. One may also combine the first and second gas supplies if the gases are such that mixing is desired.

The second gas supply system includes a source of a precursor gas 44, a remote activation chamber 46 which is located outside and at a distance from the deposition chamber, a power source 48 for activating the precursor gas within the remote activation chamber, an electronically operated valve and flow control mechanism 50 and a conduit or pipe 57 connecting the remote chamber to the deposition chamber.

A flow restrictor 59 is employed in pipe 57. Flow restrictor 59 may be placed anywhere in the path between remote chamber 46 and deposition chamber 10. Such a flow restrictor allows a pressure differential to be present between remote chamber 46 and deposition chamber 10.

The valve and flow control mechanism 50 delivers gas from the source of precursor gas 44 into the remote activation chamber 46 at a user-selected flow rate. The power source 48 activates the precursor gas to form a reactive species which is then flowed through the conduit 57 into the deposition chamber via inlet port 33. In other words, the upper electrode or shower head 12 is used to deliver the reactive gas into the deposition chamber. In the described embodiment, the remote chamber is a sapphire tube and the power source is 2.54 GHz microwave energy with its output aimed at the sapphire tube.

Optionally, there may also be a source of a minor carrier gas 52 that is connected to the remote activation chamber through another valve and flow control mechanism 53. The minor carrier gas aids in the transport of the activated

species to the deposition chamber. It can be any appropriate nonreactive gas that is compatible with the particular cleaning process with which it is being used. For example, the minor carrier gas may be argon, nitrogen, helium, hydrogen, or oxygen, etc. In addition to aiding in the transport of activated species to the deposition chamber, the carrier gas may also assist in the cleaning process or help initiate and/or stabilize the plasma in the deposition chamber.

In the described embodiment, the precursor gas is  $\text{NF}_3$ . The flow rate of activated species is about 2 liters per minute and the process chamber pressure is about 0.5 Torr. To activate the precursor gas, the microwave source delivers about 3,000–12,000 Watts to the remote activation chamber. A value of 5,000 Watts may be used for many applications.

The remote activation chamber is held at a pressure which is as high as feasible. In other words, the pressure differential between the remote chamber and the deposition chamber may be made as large as possible and may be at least, e.g., 4.5 Torr. The pressure in the remote chamber may be higher, for example, about 5 Torr to about 20 Torr, and in particular may be about 15 Torr. The pressure in the deposition chamber may be, for example, about 0.1 Torr to about 2 Torr, and in particular about 0.5 Torr. Flow restrictor 59 is employed to allow a high pressure plasma to be maintained without detrimentally affecting the pressure of deposition chamber 10. Flow restrictor 59 may be, for example, a small orifice or a series of small orifices, although any device that creates a pressure differential, such as a reduction valve or a needle valve, could be employed. Flow restrictor 59 may be placed at or near the point at which pipe 57 enters deposition chamber 10.

This choice of power and pressure for the remote chamber has several advantages. First, the high power chosen causes a practically complete activation of gases in the remote chamber, resulting in a lesser amount of precursor gases pumped out of the chamber which have adverse environmental impacts.

Second, the inventors have discovered that the percentage amount of activation is far greater than would be expected. Referring to FIG. 2, the percentage of gas breakdown (or activated gases) is shown graphed versus applied power at a pressure of 15 Torr. With a different scaling, the curve would appear much the same for the cleaning rate. As can be seen at low power, the gas breakdown is approximately linear. The inventors have discovered that at high power, such as above 2,000 Watts, the gas breakdown percentage goes through a nonlinear transitional section before asymptotically approaching 100% breakdown. This is seen in the curve having filled-in data points which is denoted MW RPS (microwave remote power source). This results in far greater gas breakdown than expected. It should be noted that the precise position of the transitional region also depends on factors such as gas pressure and gas flow.

The power ranges discussed above may be considered to be partly dependent on the size of the remote chamber. A power range of about 3,000–12,000 Watts is based on a remote chamber volume of  $\frac{1}{4}$  liter and corresponds to a power density of about 12,000–48,000 Watts/liter. These values scale both up and down for chambers of other sizes.

A third reason why the power and pressure ranges are advantageous is that the high pressure plasma is more localized. Therefore, the high pressure plasma may be less likely to diffuse out of the remote chamber and cause burning, particularly of the piping connecting the remote chamber to the deposition chamber.

A fourth reason why the power and pressure ranges are advantageous is the plasma stability. High power microwave

plasmas are more stable than low power plasmas and are easier to tune. For example, low power plasmas require a complicated automatic tuning procedure during the initiation of the plasma. If this is not used, the low power plasma will extinguish. If high power is used to initiate the plasma, an easier fixed tuning procedure may be used for both initiation and optimized tuning.

Therefore, the combination of a high power and high pressure plasma in the remote plasma activation chamber leads to an unexpectedly efficient, localized and stable plasma.

By using  $\text{NF}_3$  as the feed gas, we have been able to clean chambers that have been deposited with silicon (Si), doped silicon, silicon nitride ( $\text{Si}_3\text{N}_4$ ) and silicon oxide ( $\text{SiO}_2$ ). The cleaning rate for as-deposited film has reached 1 micron/minute for silicon nitride (flowing 2,000 sccm of  $\text{NF}_3$  at a remote chamber pressure of 15 Torr, a remote chamber power of 5,000 Watts and a susceptor temperature of 360° C.) and 1 micron/minute for, e.g., silicon nitride. These cleaning rates are faster, e.g., twice as fast, than the conventional cleaning process which employs only a local plasma with a power level of about 3 kilowatts at 13.56 MHz RF.

In general, the reactive gases may be selected from a wide range of options, including the commonly used halogens and halogen compounds. For example, the reactive gas may be chlorine, fluorine or compounds thereof, e.g.,  $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ . Of course, the particular gas that is used depends on the deposited material which is being removed. For example, in a tungsten deposition system a fluorine compound gas is typically used to etch and/or remove clean the deposited tungsten.

It should be understood that the power levels, flow rates, and pressures that are chosen are system specific and thus they will need to be optimized for the particular system in which the process is being run. Making the appropriate adjustments in process conditions to achieve optimum of performance for a particular system is well within the capabilities of a person of ordinary skill in the art.

Although the described embodiment involved a PECVD system, the invention has far wider applicability. For example, the concept of a remote activation source (i.e., outside the main vacuum chamber), possibly used in conjunction with a local activation source (i.e., inside the main vacuum chamber) can be used in systems designed for any of the following purposes: PVD, CVD, ion doping, photoresist stripping, substrate cleaning, plasma etching.

Other embodiments are within the following claims.

What is claimed is:

1. A method for cleaning a deposition chamber that is used in fabricating electronic devices, said method comprising: delivering a precursor gas into a remote chamber that is outside of the deposition chamber; activating the precursor gas in the remote chamber to form a reactive species using power from about 3,000 Watts to 12,000 Watts; flowing the reactive species from the remote chamber into the deposition chamber; and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.
2. The method of claim 1 wherein the step of activating the precursor gas is performed by using a remote activation source.
3. The method of claim 2 wherein the precursor gas is selected from the group of gases consisting of all halogens and gaseous compounds thereof.

4. The method of claim 3 wherein the precursor gas is selected from the group of gases consisting of chlorine, fluorine, and gaseous compounds thereof.

5. The method of claim 4 wherein the precursor gas is  $\text{NF}_3$ .

6. The method of claim 2 wherein the remote activation source is a microwave energy source.

7. The method of claim 2 further comprising flowing a carrier gas into the remote activation chamber.

8. The method of claim 7 wherein the carrier gas is selected from the group of gases consisting of nitrogen, argon, helium, hydrogen, and oxygen.

9. A method of cleaning a process chamber, said method comprising:

delivering a precursor gas into a remote chamber that is outside of the process chamber so that there is a pressure differential between said remote chamber and said process chamber;

activating the precursor gas in the remote chamber and to thereby form a reactive species using power from about 3,000 Watts to 12,000 Watts;

flowing the reactive species from the remote chamber into the process chamber.

10. The method of claims 1 or 9, further comprising the step of:

using a local activation source to further excite the reactive species that has been flowed into the process chamber from the remote chamber; and

using the reactive species that has been further excited by the local activation source in performing the cleaning process in the process chamber.

11. The method of claim 9, wherein said pressure differential is at least 4.5 Torr.

12. The method of claim 9, wherein the pressure in the remote chamber is between 5 Torr and 20 Torr.

13. The method of claim 12, wherein the pressure in the remote chamber is at least about 15 Torr.

14. A deposition apparatus assembly, comprising:  
a deposition chamber;

a remote chamber that is outside of said deposition chamber;

an activation source adapted to deliver energy into said remote chamber;

a first conduit for flowing a precursor gas from a remote gas supply into the remote chamber where it is activated by said activation source to form a reactive species;

a second conduit for flowing the reactive species from the remote chamber into the deposition chamber; and

a flow restrictor placed within the second conduit, whereby a pressure differential is created between said remote chamber and said deposition chamber.

15. The assembly of claim 14 further comprising a valve and flow control mechanism which controls the flow of precursor gas into the remote chamber.

16. The assembly of claim 14 wherein said flow restrictor is a reduction valve.

17. The assembly of claim 14 wherein said activation source is designed to deliver energy in a power range from about 12,000 Watts per liter to 48,000 Watts per liter.

18. The apparatus of claim 14 further comprising a valve and flow control mechanism which controls the flow of a carrier gas that is different from the precursor gas into the remote chamber.

19. A method for cleaning a deposition chamber that is used in fabricating electronic devices, said method comprising:

delivering a precursor gas into a remote chamber that is outside of the deposition chamber;

activating the precursor gas in the remote chamber to form a reactive species using power from about 12,000 Watts per liter to 48,000 Watts per liter of remote chamber volume;

flowing the reactive species from the remote chamber into the deposition chamber under a pressure differential; and

using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

20. The method of claim 19, wherein the pressure differential is at least about 4.5 Torr.

21. A method for cleaning a deposition chamber that is used in fabricating electronic devices, said method comprising:

delivering a precursor gas into a remote chamber that is outside of the deposition chamber;

activating the precursor gas in the remote chamber to form a reactive species using power from about 3,000 Watts to 12,000 Watts using a fixed tuning high power plasma source;

flowing the reactive species from the remote chamber into the deposition chamber; and

using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

\* \* \* \* \*





(10) Patent No.: US 6,274,058 B1  
(45) Date of Patent: Aug. 14, 2001

- |           |        |               |
|-----------|--------|---------------|
| 5,008,593 | 4/1991 | Schlie et al. |
| 5,082,517 | 1/1992 | Moleshi       |

- (List continued on next page.)

- FOREIGN PATENT DOCUMENTS

- |            |         |      |
|------------|---------|------|
| 03739895A1 | 6/1988  | (DE) |
| 04107329A1 | 9/1991  | (DE) |
| 04132561A1 | 4/1993  | (DE) |
| 04202862A1 | 8/1993  | (DE) |
| 0343038A1  | 5/1988  | (EP) |
| 3443038A1  | 11/1989 | (EP) |
| 0697467A1  | 10/1995 | (EP) |
| 61-14726   | 1/1986  | (JP) |
| 63-48832   | 3/1988  | (JP) |
| 1-102921   | 4/1989  | (JP) |
| 2-125872   | 5/1990  | (JP) |
| 4-100221   | 4/1992  | (JP) |
| 4-137618   | 5/1992  | (JP) |
| 4-165075   | 6/1992  | (JP) |
| 5-90180    | 4/1993  | (JP) |
| 5-90426    | 4/1993  | (JP) |
| 6-318580   | 11/1994 | (JP) |
| 8-85885    | 4/1996  | (JP) |

- (22) Filed: Jul. 2, 1999

### Related U.S. Application Data

- Primary Examiner—Thi Dang*

- (74) *Attorney, Agent, or Firm*—Blakely Sokoloff Taylor & Zafman

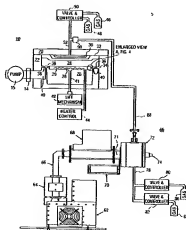
- (57) ABSTRACT

- A processing chamber cleaning method is described which utilizes microwave energy to remotely generate a reactive species to be used alone or in combination with an inert gas to remove deposits from a processing chamber. The reactive species can remove deposits from a first processing region at a first pressure and then remove deposits from a second processing region at a second pressure. Also described is a cleaning process utilizing remotely generated reactive species in a single processing region at two different pressures. Additionally, different ratios of reactive gas and inert gas may be utilized to improve the uniformity of the cleaning process, increase the cleaning rate, reduce recombination of reactive species and increase the residence time of reactive species provided to the processing chamber.

- (56)
- References Cited**

## U.S. PATENT DOCUMENTS

- |           |         |                   |
|-----------|---------|-------------------|
| 4,433,228 | 2/1984  | Nishimatsu et al. |
| 4,576,692 | 3/1986  | Fukuta et al.     |
| 4,736,304 | 4/1988  | Doehler.          |
| 4,831,963 | 5/1989  | Saito et al.      |
| 4,898,118 | 2/1990  | Murakami et al.   |
| 4,909,184 | 3/1990  | Fujiyama.         |
| 4,946,549 | 8/1990  | Bachman et al.    |
| 4,960,071 | 10/1990 | Akahori et al.    |
| 4,986,214 | 1/1991  | Mumoto et al.     |
| 4,996,077 | 2/1991  | Moslehi et al.    |

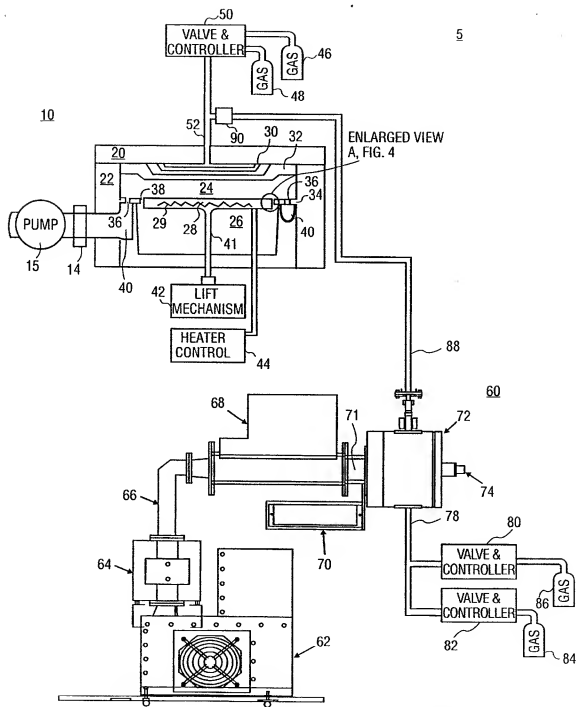


## APPENDIX B

Appl. No.: 10/759,953

## U.S. PATENT DOCUMENTS

5,084,126	1/1992	McKee .	5,413,670	5/1995	Langan et al. .
5,111,111	5/1992	Stevens et al. .	5,449,434	9/1995	Hooke et al. .
5,133,825	7/1992	Hakamata et al. .	5,451,615	9/1995	Krogh .
5,134,965	8/1992	Tokuda et al. .	5,454,903	10/1995	Redeker et al. .
5,158,644	10/1992	Cheung et al. .	5,462,602	10/1995	Misiano et al. .
5,173,641	12/1992	Imahashi et al. .	5,466,991	11/1995	Berry .
5,211,796	5/1993	Hansen .	5,474,615	12/1995	Ishida et al. .
5,211,995	5/1993	Kuehnle et al. .	5,489,362	2/1996	Steinhardt et al. .
5,234,526	8/1993	Chen et al. .	5,491,112	2/1996	Buchta et al. .
5,234,529	8/1993	Johnson .	5,503,676	4/1996	Shufflebotham et al. .
5,266,364	11/1993	Tamura et al. .	5,520,771	5/1996	Kanai et al. .
5,282,899	2/1994	Balmashnov et al. .	5,540,812	7/1996	Kadomura .
5,306,985	4/1994	Berry .	5,545,289	8/1996	Chen et al. .
5,364,519	11/1994	Fujimura et al. .	5,558,717	9/1996	Zhao et al. .
5,387,288	2/1995	Shiaus .	5,567,241	10/1996	Tsu et al. .
5,401,358	3/1995	Kadomura .	5,611,863	3/1997	Miyagi .
5,405,492	4/1995	Molschi .	5,626,679	5/1997	Shimizu et al. .



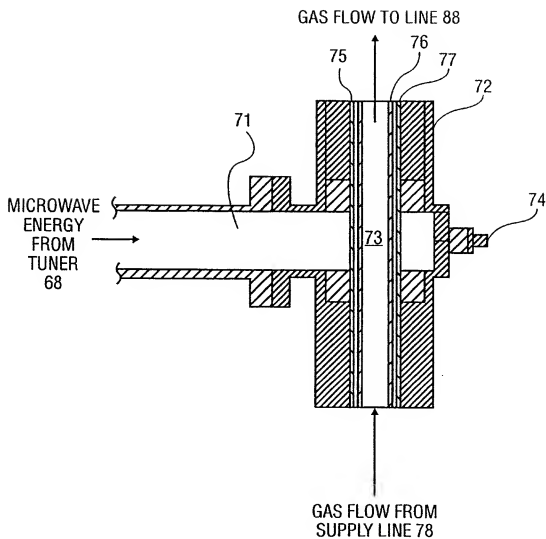


FIG. 2

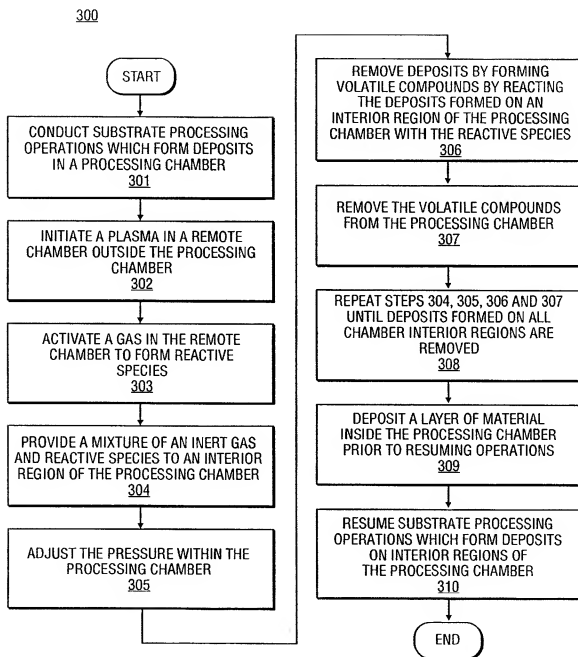


FIG. 3

ENLARGED VIEW A

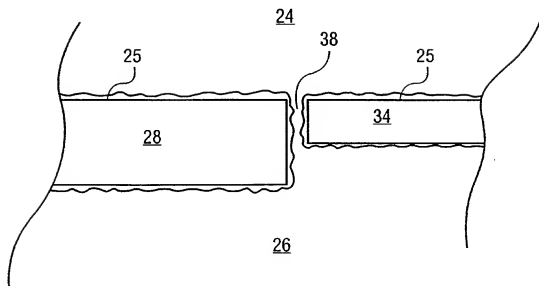


FIG. 4

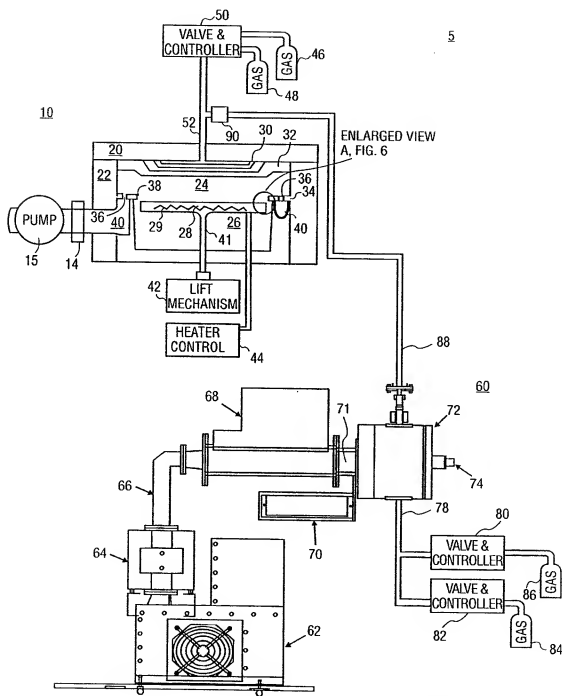


FIG. 5

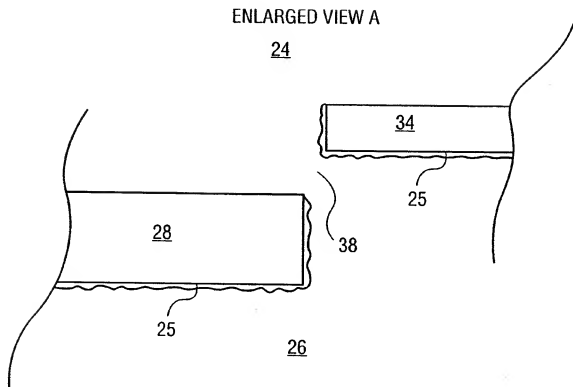


FIG. 6



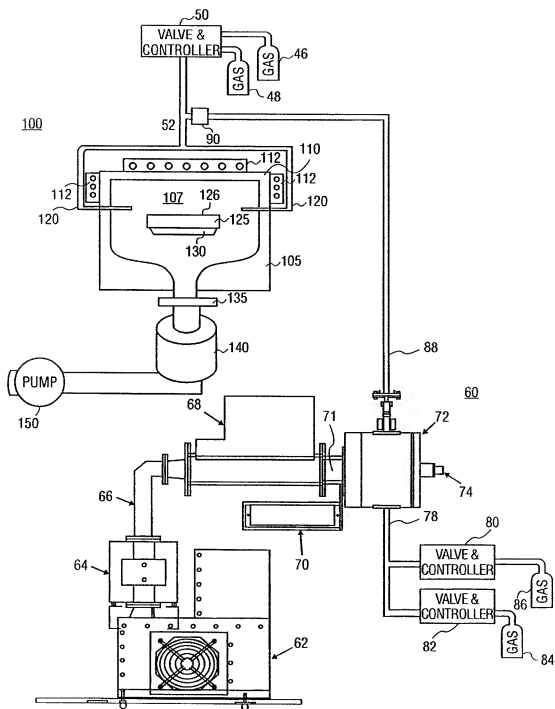


FIG. 7

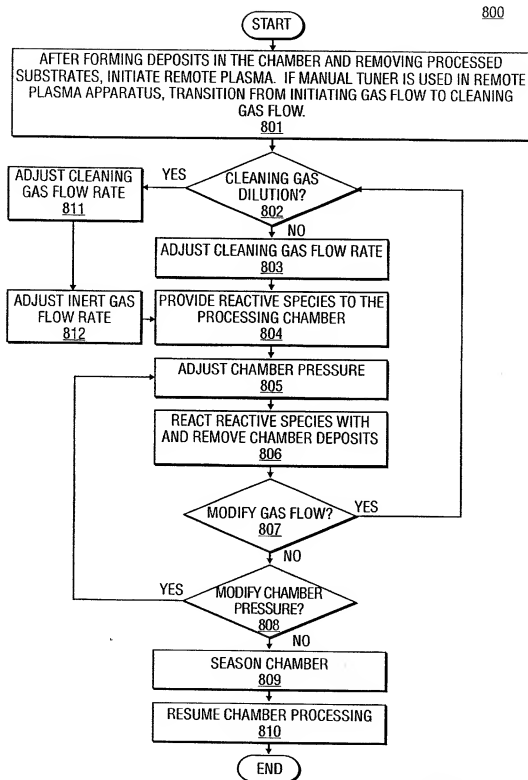


FIG. 8

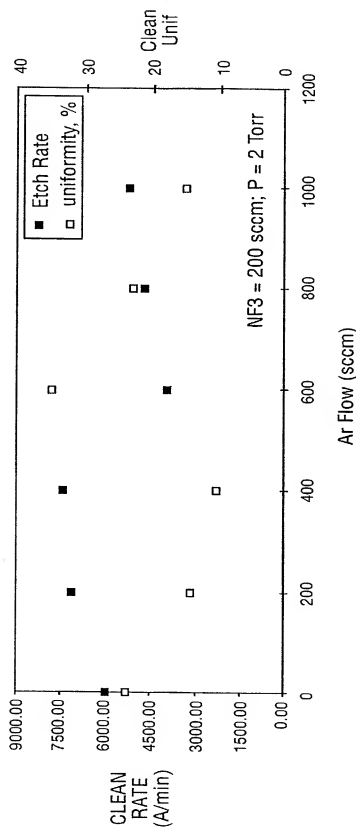


FIG. 9

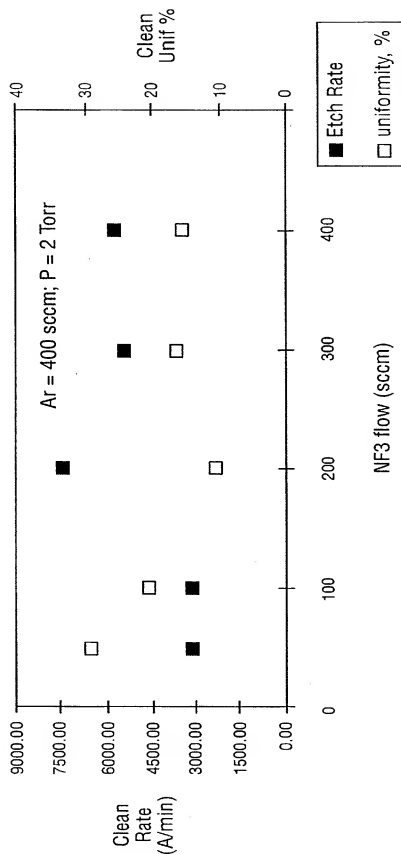


FIG. 10

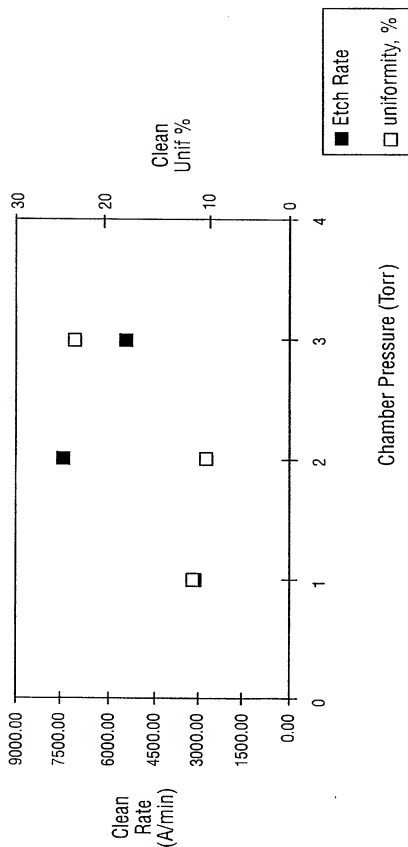
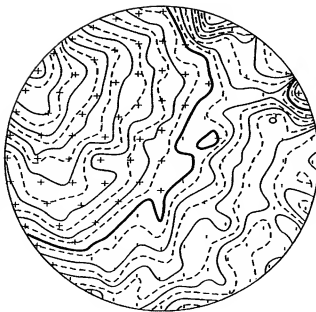


FIG. 11

## Clean Rate and Uniformity with Ar:NF3 = 1:2

NANOMETRICS 2D MAP



Cln rate = 2000 A/min

Ar:NF3 = 2:1

NF3 = 1500 sccm

P = 4500 W

MEAN: 5974 Å  
St Dev: 259.4 Å  
St Dev%: 4.34%  
UNIF: 9.42%  
MAX: 6646 Å  
MIN: 5520 Å  
RANGE<sup>α</sup>: 1120 Å  
INTERVAL: 45.0 Å

With Ar:NF3 = 1:2 (750/1500sccm) a clean rate of 2000A/min Unif = 4.5% was obtained

FIG. 12

# 1

## REMOTE PLASMA CLEANING METHOD FOR PROCESSING CHAMBERS

### FIELD OF THE INVENTION

This application is a continuation-in-part of application Ser. No. 08/893,922 entitled "Improved Cleaning Process" filed Jul. 11, 1997 and commonly assigned to Applied Materials, Inc. now U.S. Pat. No. 6,125,859.

This invention relates generally to methods and apparatuses suitable for removing accumulated processing by-products and unwanted deposits within processing reactors. More particularly, this invention relates to a method for cleaning the internal components of a wafer processing apparatus after the deposition of Tantalum containing films, such as Tantalum Pentaoxide ( $Ta_2O_5$ ). Additionally, the method described is suitable for removing deposits formed by other processes useful in the manufacture of semiconductor devices and flat panel displays.

### BACKGROUND OF THE INVENTION

The desire for greater capacity integrated circuits (ICs) on smaller sized devices has increased interest in replacing today's 64 megabit DRAM with memory devices in the range of 256 megabit, 1 gigabit and higher. This need for increased capacity on the same or smaller substrate footprint device makes it necessary to replace conventional dielectric films previously used in stacked capacitor formation, such as silicon dioxide ( $SiO_2$ ), with dielectric films having higher dielectric constants. Capacitors containing high-dielectric constant materials, such as  $Ta_2O_5$ , usually have much larger capacitance densities than standard  $SiO_2-Si_3N_4-SiO_2$  stack capacitors making them the materials of choice in IC fabrication. High dielectric constant films allow smaller capacitor areas which in turn enable closer spacing of transistors and increased transistor density. One material of increasing interest for stack capacitor fabrication is Tantalum Pentaoxide which has a relative dielectric constant more than six times that of  $SiO_2$ . Accompanying the increased and expanding use of this material is a need for improved in-situ methods of removing unwanted deposits which accumulate within the processing chamber after repeated deposition cycles.

An available cleaning method involves the utilization of a remote plasma generator to produce reactive species which are delivered to the processing chamber. U.S. Pat. No. 5,449,411 issued Sep. 12, 1995, to Hitachi describes a process for cleaning a vacuum chamber prior to the deposition of  $SiO_2$  therein. A microwave plasma of process gases such as  $C_2F_6$ ,  $CF_4$ ,  $CHF_3$ ,  $CH_4$ ,  $F_2$ ,  $HF$ ,  $Cl_2$  or  $HCl$  is described. The patent further describes that the cleaning process can be improved by applying an R.F. electric field to electrodes in the chamber.

U.S. Pat. Nos. 5,778,788 issued Aug. 4, 1998, to Applied Komatsu Technology, describes a method for cleaning a deposition chamber that is used in fabricating electronic devices by activating a precursor gas using a high power microwave source of between about 3,000 to 12,000 Watts or a power density in the remote chamber of about 12,000 Watts/liter to 48,000 Watts/Liter. The patent further describes a minor carrier gas such as Argon, nitrogen, helium, hydrogen or oxygen may be used to transport the reactive species to the chamber, assist in the cleaning process, or help initiate and/or stabilize the plasma in the deposition chamber. The patent also describes the use of a chamber based excitation source used to further excite the reactive species provided to the chamber.

# 2

Another problem confronting the semiconductor industry is the increased cost to obtain process gases coupled with the increased costs of disposing of the exhaust by-products created by process gases. The cleaning gas  $NF_3$  is an illustrative example of this problem. Long recognized as a superior cleaning gas, the cost of purchasing  $NF_3$  has steadily increased. What is needed is an improved remote plasma chamber cleaning process which utilizes cleaning gases more efficiently resulting in an overall decrease in gas consumption. The improved process should rely solely on remote microwave excitation sources without requiring chamber based excitation to produce an effective plasma or remove chamber deposits. The decreased gas consumption lowers gas supply cost, CFC generation and gas disposal cost. More specifically, the improved method should be capable of providing commercially viable cleaning rates for dielectric films such as  $Ta_2O_5$ , and other dielectric films.

### SUMMARY OF THE INVENTION

An embodiment of the present invention is a method of cleaning from a processing chamber deposits formed on interior surfaces of the processing chamber wherein said processing chamber interior surfaces include a first region and a second region said second region being different from said first region, said method comprising the steps of: dissociating a gas mixture outside said processing chamber to form reactive species, said gas mixture comprising an inert gas and a cleaning gas; providing said reactive species to said processing chamber; reacting said reactive species with said deposits in said processing chamber first region; forming volatile compounds from said deposits formed in said processing chamber first region; removing from said processing chamber said volatile compounds formed from deposits formed in said processing chamber first region; increasing the fluid communication between said processing chamber first and second regions; reacting said reactive species with said deposits in said processing chamber second region; forming volatile compounds from said deposits formed in said processing chamber second region; and removing from said processing chamber said volatile compounds formed from deposits formed in said processing chamber second region.

Another embodiment of the present invention is a method of removing deposits formed in a processing chamber as a result of deposition operations performed on a substrate disposed within the processing chamber, the method comprising the steps of activating a cleaning gas in a remote chamber separate from said processing chamber to form reactive species from said cleaning gas; providing an inert gas which mixes with said reactive species to form a gas mixture comprising reactive species; providing said gas mixture to said processing chamber while maintaining said processing chamber at a first pressure; while maintaining said processing chamber at said first pressure, reacting said reactive species with said deposits to form volatile compounds and thereafter removing from said processing chamber said volatile compounds formed at said first pressure; providing said gas mixture comprising reactive species to said processing chamber while maintaining said processing chamber at a second pressure that is different from said first pressure; while maintaining said processing chamber at said second pressure, reacting said reactive species with said deposits to form volatile compounds and thereafter removing from said processing chamber said volatile compounds formed at said second pressure; and conducting processing operations in said processing chamber to form a film on interior surfaces of said processing chamber without a substrate disposed within said chamber.

## BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 is a cross sectional and schematic view of a processing system of the present invention.

FIG. 2 is a cross sectional view of a remote plasma applicator cavity.

FIG. 3 is a block diagram illustrating a method of the present invention.

FIG. 4 is enlarged view A of FIG. 1.

FIG. 5 is a cross sectional and schematic view of a processing system of the present invention;

FIG. 6 is enlarged view A of FIG. 4.

FIG. 7 is a cross sectional and schematic view of a single volume processing chamber and the remote plasma apparatus of the present invention.

FIG. 8 is a block diagram illustrating a method of the present invention.

FIG. 9 is a graph illustrating the effect of Argon flow on cleaning rate and cleaning uniformity.

FIG. 10 is a graph illustrating the effect of NF<sub>3</sub> flow on cleaning rate and cleaning uniformity.

FIG. 11 is a graph illustrating the effect of chamber pressure on cleaning rate and uniformity.

FIG. 12 is a thickness map of a 300 mm wafer exposed to a cleaning method according to the present invention.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a novel in-situ cleaning process for removal of accumulated processing by-products on interior surfaces of a processing chamber. The described embodiment uses a resistively heated CVD chamber. One example of this type of chamber is an xZ style single wafer processing chamber manufactured by Applied Materials, modified as described herein. The chamber described is part of a modular processing system which can be utilized for a wide variety of semiconductor processing technologies such as the thermal deposition of Tantalum Pentaoxide (Ta<sub>2</sub>O<sub>5</sub>). Although the description and embodiments which follow are described with relation to the deposition and cleaning of Ta<sub>2</sub>O<sub>5</sub> comprising films, one skilled in the art will appreciate that the methods set forth in the present invention are adaptable to commercially available processing systems and operations without departing from the scope of the present invention. In some instances, well known semiconductor processing equipment and methodology have not been described in order not to unnecessarily obscure the present invention.

FIG. 1 is a schematic view of a processing system 5 of the present invention which contains processing chamber 10 and remote plasma generator 60. Processing chamber 10 is comprised of a lid 20 and chamber body 22 which together form an evacuable, temperature controlled processing environment. Lid 20 and chamber body 22 are typically made from rigid materials having good thermal characteristics. For example, chamber lid 20 and body 22 could be formed from aluminum.

In the representative embodiment shown in FIG. 1, a resistively heated substrate support 28 is provided within chamber 10 to support a workpiece and provide the heat of reaction for a thermal deposition reaction such as, for example, the deposition of Ta<sub>2</sub>O<sub>5</sub> by decomposition of Tantalum precursors such as Ta(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> or TAETO and Tantalum Tetraethoxide Dimethylaminoethoxide (Ta(OEt)<sub>4</sub>(OC<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>N(Me)<sub>2</sub>) or TAT-DMAE. Power provided to

resistive heater 29 within substrate support 28 is adjusted by heater controller 44. Power to heater 29 is adjusted to provide adequate temperature for the desired processing operation to be performed within chamber 10. The vertical position of substrate support 28 within chamber 10 is controlled by lift mechanism 42. Support shaft 41 couples substrate support 28 to lift mechanism 42. The position of substrate support 28 within chamber 10 or spacing is the separation between the lower surface of showerhead 32 and the upper surface of substrate support 28. Spacing is measured in thousandths of an inch or mils with larger spacing indicating increasing separation between showerhead 32 and substrate support 28. Components within chamber 10 typically have a protective coating or are fabricated from durable materials which tolerate exposure to the relatively high temperatures and often caustic chemical environments used in the fabrication of electronic components. For example, showerhead 32 could be formed from aluminum. Graphite and ceramic compositions are often employed in the fabrication of substrate supports 28 and support shafts 41.

Pump 15 and throttle valve 14 are used in conjunction to evacuate chamber 10 and provide a pressure regulated environment within chamber 10. Pump 15 is in communication with pumping channel 40 located in the periphery of walls 22 and encircling substrate support 28. Pumping plate 34 is provided with a plurality of apertures 36 which provide more uniform conduction and evacuation of chamber interior regions 24 and 26. Spacing 38 separates substrate support 28 from pumping plate 34. For the representative chamber 10 of FIG. 1, spacing 38 is between about 0.112 inches and 0.088 inches. Thus, substrate support 28 and pumping plate 34 in effect divide the interior of chamber 10 into an upper interior region 24 and a lower interior region 26. Upper interior region 24 also includes showerhead 32 and gas distribution plate 30.

Processing gases are stored outside chamber 10 in gas supplies 46 and 48. Valve and controller 50 represents an electronic metering and control system such as a mass flow controller used to introduce gases into chamber 10. From valve and controller 50, gases from supplies 46 and 48 flow through chamber supply piping 52, lid 20, gas distribution plate 30 and showerhead 32 before entering interior chamber regions 24 and 26. Although shown using a single valve and controller 50, gas supplies 46 and 48 could also be controlled by independent valve and controller unit 50 depending upon the process desired within chamber 10.

Also illustrated in FIG. 1 is remote plasma generating system 60 which is used to activate gases and provide the resulting reactive species to chamber interior regions 24 and 26. One advantage of a remote plasma generator 60 is that the generated plasma or reactive species created by remote plasma generator 60 may be used for cleaning or process applications within internal chamber processing regions 24 and 26 without subjecting internal chamber components such as substrate support 28, shower head 32, or pumping plate 34 to ion bombardment which usually results when RF energy is applied within interior processing regions 24 and 26 to create a plasma. Reactive species generated by remotely activated plasma are considered less damaging since they do not subject internal chamber components to ion bombardment.

Another advantage of a remote excitation cleaning method of the present invention over some chamber based excitation cleaning methods is that in a remote excitation cleaning method the chamber conditions, such as temperature, may be maintained at or near the conditions



5

associated to the process to be conducted in the chamber. For example in a representative embodiment of the present invention where the chamber is used to deposit  $Ta_2O_5$  at 475° C., remotely activated species may be provided to the chamber at the same temperature thereby eliminating the extra time required to change chamber temperature between the deposition process and the remotely activated cleaning process.

Turning now to the schematic illustration of remote plasma generator 60 which appears in FIG. 1, the components and operation of remote plasma apparatus 60 of the present invention can be better appreciated. Magnetron assembly 62 houses the magnetron tube, which produces the microwave energy. A representative magnetron tube 62 consists of a hot filament cylindrical cathode surrounded by an anode with a vane array. This anode/cathode assembly produces a strong magnetic field when it is supplied with DC power from a power supply. Electrons coming into contact with this magnetic field follow a circular path as they travel between the anode and the cathode. This circular motion induces voltage resonance, or microwaves, between the anode vanes. An antenna channels the microwaves from magnetron 62 to isolator 64 and wave guide 66. Isolator 64 absorbs and dissipates reflected power to prevent damage to magnetron 62. Wave guide 66 channels microwaves from isolator 64 into tuner 68.

Tuner 68 matches the impedance of magnetron 62 and microwave cavity 72 to achieve the minimum degree of reflected power by adjusting the vertical position of three tuning stubs located inside wave guide 66. Tuner 68 could be adjusted manually or automatically. If an automatic tuner is employed with tuner 68, a feedback signal can be provided to the magnetron power supply in order to continuously match the actual forward power to the setpoint. Auto tuner controller 70 controls the position of the tuning stubs within wave guide 66 to minimize reflected power. Auto tuner controller 70 also displays the position of the stubs as well as forward and reflected power readings.

If a manual tuner is used, the positions of the stubs could be set manually and adjusted as needed to minimize reflected power. Although more expensive than manual tuner controllers, automatic tuner controllers can strike and sustain a plasma with a cleaning gas such as, for example,  $NF_3$ . Since it is more difficult to strike and sustain a plasma with only a cleaning gas generally an automatic tuner controller is required. With manual tuners, an extra plasma initiation step may be required where an inert gas is flowed through the remote apparatus and the plasma struck. Once the plasma is formed in the applicator with an inert gas, the cleaning gas is introduced. Finally, the flow rate of the cleaning gas is increased to the desired flow condition while the inert gas flow is decreased until the desired gas flow or gas composition is obtained.

Turning now to FIG. 2 which shows a cross section of microwave applicator cavity 72 where gases from supply line 78 are exposed to microwave energy from magnetron 62. Applicator 72 has a cylindrically shaped sapphire tube 76 located within another cylindrically shaped quartz tube 75. In order to prevent overheating and damage to tubes 75 and 76, cooling water is provided to cooling wave channel 77 which separates tubes 75 and 76. Microwave energy exiting tuner 68 travels through microwave channel 71 which is coupled to applicator 72 and positioned such that exiting microwaves are directed towards tubes 75 and 76. Activation volume 73 is formed by the intersection of the cross section of channel 71 and sapphire tube 76. For example, activation volume 73 is about  $4.733 \times 10^{-3}$  liters in an

6

embodiment where microwave channel 71 has a rectangular cross section with a height of about 3.4 inches and a width of about 1.7 inches while tube 76 has an inner diameter of 1.04 inches. Representative microwave power settings of between 1400–3200 Watts result in a power density of between 295,800 W/L to 676,100 W/L within activation volume 73. The power density is scalable and will vary depending on specific geometry of the system and the microwave power utilized. Although described as rectangular and cylindrical, one of ordinary skill in the art will appreciate that other shapes can be employed in microwave channel 71 as well as tubes 75 and 76. Although described as fabricated from sapphire and quartz respectively, tubes 76 and 75 may also be formed from other suitable materials capable of sustained exposure to microwave energy. Additionally, inner tube 76 should be inert to the gases provided from supply line 78.

Gas or gases supplied via gas supply line 78 enter water cooled sapphire tube 76 within microwave applicator 72. The gas or gases subjected to the microwave energy ionizes producing reactive species which can then be used in cleaning and processing operations within processing chamber 10. For example, one such cleaning gas is  $NF_3$  which can be used to supply reactive fluorine for cleaning processing chamber interior regions 24 and 26 when a substrate is not present in chamber 10. The microwave power level is one limit on the amount of reactive species created. For example, a microwave power level of about 3500 W is capable of completely dissociating about 1700 sccm of  $NF_3$ . Gas flows above 1700 sccm may result in incomplete cleaning gas dissociation. An optical plasma sensor 74 detects the existence of plasma within cavity 72. Reactive species generated within microwave applicator cavity 72 are supplied to chamber 10 via chamber supply line 88.

Referring again to FIG. 1, reactive species within chamber supply line 88 pass control valve 90 which could be an on/off valve or part of a diverter valve system. Employing a diverter in valve 90 allows for the continued operation of remote plasma generator while not requiring that reactive species be provided to chamber 10. Once past control valve 90, reactive species from remote plasma generator 60 flow through gas supply line 52, lid 20, gas distribution plate 30 and showerhead 32 before entering chamber interior regions 24 and 26.

Gases to be dissociated in remote plasma generator 60 are stored in gas supplies 86 and 84. Valve and control mechanisms 80 and 82 represent electronic flow control units for gas supplies 86 and 84 respectively. The output setpoint of valve and flow control mechanisms 80 and 82 is determined by the user and the resulting gas flow output is provided to microwave applicator cavity 72 via supply piping 78. In accordance with the present invention, gas supply 84 could be a source of cleaning gas to be dissociated into reactive species for the removal of deposits formed within chamber 10. Although the present embodiment will be described with respect to the use of  $NF_3$ , the reactive gas or cleaning gas may be selected from a wide variety of halogens and halogen compounds. For example, the reactive gas may be chlorine, fluorine or compounds thereof, e.g.  $NF_3$ ,  $CF_4$ ,  $SF_6$ ,  $C_2F_6$ ,  $CCl_4$ ,  $C_2Cl_6$ . Reactive gas selection will depend upon the material to be removed. For example, reactive fluorine may be used to remove or clean accumulations of  $Ta_2O_5$  as set forth in a representative embodiment of the present invention.

Also in accordance with the present invention, gas supply 86 is a source of inert gas with a two fold purpose. For those microwave generator apparatus 60 having a manual tuner

60, an inert gas is used to initiate the plasma within microwave applicator cavity 72. Second, in accordance with the ratios described below, the inert gas is flowed concurrently with the reactive gas in order to prevent reactive species recombination thereby increasing the number of reactive species which reach chamber 10. The addition of an inert gas also increases the residence time of those reactive species within chamber 10. Although the ratio between the inert gas and the cleaning or reactive gas is described in relation to flow rates, the ratio of cleaning gas to inert gas could also be determined by any other means to describe the relative amounts of each gas provided to chamber 10.

Although gas supply 78 is illustrated in FIGS. 1, 5 and 7 as flowing inert gas through applicator 72, it is to be understood that the inert gas could instead be provided to the flow of reactive species at supply line 88. Providing the inert gas into the flow of reactive species down stream of applicator 72 has the additional advantage of increasing the amount of power applied to the cleaning gas flow within applicator 72 since only the cleaning gas flows through applicator 72.

The present invention can be carried out in a processing chamber modified to operate in conjunction with a remote plasma generating source as illustrated in FIG. 1. FIG. 3 contains block diagram 300 which sets forth the novel cleaning process of the present invention. The remote plasma cleaning process is set forth in blocks 302-308 of FIG. 3. For purposes of illustration, the method of the present invention will be described as implemented for a processing system similar to processing system 5 of FIG. 1. Accordingly, reference numbers and components shown in FIG. 1 will be used in the description which follows.

The first step of the present invention as set forth in block 301 is to conduct processing operations which results in the formation of deposits within a processing chamber. In this illustration, the processing operation described is for the thermal deposition of tantalum pentaoxide by mixing a tantalum precursor with an oxidizing agent at approximately 450° C. A substrate is placed on resistively heated substrate support and heater controller 44 adjusts the power provided heater 29 to maintain the substrate at an appropriate processing temperature of about 450° C. Lift mechanism 42 positions substrate support 28 and the wafer thereupon in chamber 10 relative to showerhead 32 to a spacing of, for example, 400 mils. Gas supplies 46 and 48 of FIG. 1 contain an oxidizing gas such as oxygen or nitrous oxide and a tantalum precursor such as TAF-DMAE or TAETO. An inert gas such as  $N_2$  may be employed as a carrier gas for the Tantalum precursor. Valve and controller mechanism 50 mixes and adjusts the flow rate of the tantalum and oxidizing gases and delivers them to chamber 10. The temperature of the substrate positioned on support 28 is sufficient to form tantalum pentaoxide from the incoming gas stream.

Some processes necessitate cleaning after each substrate is processed. Other processes tolerate periodic cleaning after a consecutive series of processes sequences, or after the deposition of a specified film thickness. One example of periodic cleaning is the deposition of  $Ta_2O_5$  where a series of substrates are processed where each substrate receives about 100 angstroms (Å) of  $Ta_2O_5$  film. After a number of substrates have been processed in this manner, the chamber is cleaned after the last substrate is removed from the chamber. A typical processing cycle for  $Ta_2O_5$  is 500 wafers each with 100 angstroms (Å) or, alternatively, cleaning the chamber once for every 1 micron of film deposited.

Chamber 10, like other deposition chambers, are designed to preferentially deposit film on substrates positioned within

the chamber. Deposition will also occur on other surfaces within interior regions 24 and 26 with sufficient temperature to react the process gases. In a resistively heated deposition chamber such as chamber 10 which has no means other than thermal energy for activation or to drive reactions, deposition is expected on those surfaces heated because of proximity to resistively heated substrate support such as the lower surface of showerhead 32, the upper surface of pumping plate 34 and walls 32 surrounding first interior region 24. Since substrate support 34 is larger than the substrate being processed, deposition will also occur on the outer periphery of the upper surface of substrate support 34 not covered by the wafer being processed. In a periodic cleaning process cycle, accumulations vary according to the number of wafers processed and the film thickness deposited on each wafer.

FIG. 4 illustrates view A of FIG. 1 which is an enlarged view of the edges of pumping plate 34 and substrate support 28 separated by spacing 38 after the deposition process described above has taken place. Generally, FIG. 4 is representative of the chamber specific accumulations which can occur. In a representative periodic clean process, for example the deposition of  $Ta_2O_5$ , wafers are processed in series of 100 with each wafer receiving a 100 Å layer of  $Ta_2O_5$ . Such a processing cycle results in the highest accumulations, about 200 Å, on exposed areas of and the edges of pumping plate 34 nearest to substrate support 28. The thickness of the accumulation on other chamber components varies according to the temperature of the component and the degree of exposure to process gases.

The apparent division of chamber 10 into interior regions 24 and 26 by pumping plate 34 and substrate support 28 is illustrative of the obstruction of certain chamber internal regions by the interrelation of internal chamber components. Thus, the narrow spacing 38 between pumping plate 34 and substrate support 28 results in interior regions 24 and 26. The narrow spacing 38 is an area of reduced fluid communication between interior regions 24 and 26. Narrow spacing 38 is representative of an interference which occurs within processing chamber 10 such that the reaction conditions interior to the chamber beyond the preferred deposition region 24 will be dissimilar. Obstructions and restrictions like spacing 38 are not limited to resistively heated chambers such as chamber 10 but also found in other processing chambers as well. Examples from other processing apparatus where obstructions form different regions within a processing area include: portions of the horizontal position mechanism of a horizontal feed tube reactor are obstructed by the quartz boat used within the reactor so that the manner in which a quartz wafer boat utilized in a tube reactor obstructs those portions of the tube blocked by the apparatus which moves the boat; shadow rings used in some etch processes have surfaces which are not exposed to reactant gases and conversely surfaces which are exposed to and may accumulate the etched material; and substrate handling systems may result in lift mechanisms which can obstruct or otherwise restrict portions of a processing chamber.

Thus, in the specific embodiment of FIG. 1, chamber 10 is divided into first interior region 24 and second interior region 26. As a result of spacing 38 with support 28 nearly in plane with pumping plate 34, the effective chamber volume of first interior region 24 is approximately 0.6402 L.

Continuing with flow diagram 300 of FIG. 3 and as set forth in block 302, initiate a plasma within a remote plasma generator located outside of the processing chamber while there is no substrate in chamber 10. As described above, a plasma initiating gas would be utilized in a remote plasma

system 60 having a manual tuner controller. In the case of an remote plasma system 60 having an automatic tuner controller, step 302 is not required since a sustainable plasma may be initiated directly from the selected cleaning gas. The plasma initiating gas may be any of the Group vm gases, such as for example, He, Ne, Xe, and Ar, or an inert gas such as  $N_2$ , or other gas suitable for plasma initiation. Here, inert gas or plasma initiating gas refers to those gases which do not appreciably dissociate when exposed to the microwave energy at the power levels described. In a specific embodiment, gas supply 86 contains Ar and valve and control mechanism 80 adjusts the flow of Ar to about 600 standard cubic centimeters per minute (scm) which flows through supply line 76 into microwave applicator cavity 72.

Inside applicator cavity 72 the gas stream passes through a water cooled applicator tube where it is exposed to microwave energy levels of at least 100 W and preferably between about 1400 Watts and 3200 Watts generated by magnetron assembly 62. A representative microwave energy level suitable for a chamber 10 of FIG. 1 and the gas flows described is about 1400 Watts. In an embodiment where Ar is used to initiate a plasma, microwave energy passes through the sapphire tube and an Ar plasma is created within microwave applicator cavity 72. The plasma produces high energy or internally hot Ar which flows into remote plasma supply line 88, control valve 90, gas supply line 52 and into chamber 10. Chamber 10 is maintained at about 2.0 Torr while plasma is established in microwave applicator cavity 72. In those systems with a manual tuner, a typical time to initiate a remote plasma using an inert gas such as Ar and obtain a stable high energy Ar flow to chamber 10 is about 10 seconds or less.

Next, as set forth in block 303, activate a gas in the remote chamber to form reactive species. Gas supply 84 could contain a halogen bearing gas such as  $Cl_2$ , HCl,  $ClF_3$ ,  $NF_3$ ,  $SF_6$ ,  $F_2$  and HF. In the case of a remote apparatus 60 having an automatic tuner, steps 302 and 303 may be executed together since the gas to be activated could also be used to initiate the plasma. While maintaining the plasma within applicator 72, the flow rate of the gas to be activated is provided by valve and controller mechanism 82 which allows gas to flow through supply line 78 into microwave applicator cavity 72. Inside applicator cavity 72 the gas stream passes through the water cooled sapphire applicator tube where the cleaning gas stream is exposed to microwave energy generated by magnetron assembly 62 and the initiated plasma. A representative microwave energy level is about 1400 Watts. In an embodiment where  $NF_3$  is used as a cleaning gas, dissociation within applicator cavity 72 produces reactive F, some  $N_2$ , and trace amounts of NF and  $F_2$ . Using  $NF_3$  has particular advantages such as its low dissociation energy and its production of multiple reactive fluorine species from each individual  $NF_3$  molecule.

Next, as set forth in block 304, provide a mixture of inert gas and reactive species to an interior region of the processing chamber. Since microwave application cavity 72 is located remote to chamber 10, reactive species generated by remote plasma system 60 flow some distance along chamber supply line 88 to reach chamber 10. As a result, reactive species produced by dissociation with applicator cavity 72 could collide and recombine while flowing to chamber 10. Instead of providing reactive species to remove deposits formed within chamber 10, recombined and less reactive gases are provided to chamber 10. In an embodiment where  $NF_3$  is activated in applicator 72, reactive F may recombine and instead provide  $F_2$  and  $NF_2$  to chamber 10. Thus,

recombination of the reactive species before chamber 10 reduces the efficiency of remote plasma generating system 60 to provide reactive species into chamber interior regions 24 and 26. Providing an inert gas with the reactive species increases the probability that molecular collisions enroute to chamber 10 will be between reactive species and inert gas thereby reducing the probability of reactive species recombination.

In a representative embodiment where Ar is the inert gas and  $NF_3$  is the cleaning gas, the respective flow rates could be adjusted to about 200 scm  $NF_3$  and about 400 scm Ar. Maintaining about a 2:1 ratio between the inert gas and the reactive gas reduces the probability that reactive species produced by the reactive gas dissociation will recombine.

The optimal inert gas to reactive gas ratio may also vary based on the characteristics of the specific remote plasma generator utilized and the type of reactive gas employed. Advantageous results have been achieved when the inert gas to reactive gas ratio is maintained within about 25% of the 2:1 ratio described above.

Next, as set forth in block 305, is to adjust the pressure within the processing chamber. Generally, an aspect of chamber pressure is that higher pressure tends to decrease residence time of the reactive species within the chamber. However, when cleaning initially begins within region 24 the highest amounts of deposits are present. Even though the activated species have a shorter residence time and mean free path, the likelihood of activated species reacting with and removing deposits is high. It is believed that lower pressures, on the other hand, tend to lengthen the mean free path and residence time thereby allowing dispersion of the reactive species across the interior region of the chamber. In a specific embodiment of the present invention, a chamber pressure of about 2.0 Torr results in cleaning rates which are higher on the substrate support 28 or central portion of the chamber than on walls 22 or outer portion of the chamber.

Next, as set forth in block 306, is to remove deposits formed on interior regions of the processing chamber. Removing the deposits formed on the interior chamber surfaces or cleaning the chamber is accomplished by reacting the reactive species with the deposited film on the chamber surface to form a volatile compound. For example, in a chamber used for Tantalum Pentaoxide deposition such as the chamber 10 of FIG. 1,  $NF_3$  can be remotely dissociated as described above to form reactive fluorine. The reactive fluorine then reacts with and removes the Tantalum Pentaoxide formed within the interior of chamber 10. Referring to chamber 10 illustrated in FIG. 1, most of the reactive species provided to chamber 10 will react with deposits formed within interior chamber region 24. The reactive species remain mostly in the effective volume of interior region 24 because of the narrow spacing 38 between substrate support 28 and pumping plate 34. Some reactive species will interact with the tantalum pentaoxide deposits formed on the opposing edges and lower surfaces of substrate support 28 and pumping plate 34. Generally, most of the deposits removed will be those formed on surfaces within interior region 24. For example in chamber 10 of FIG. 1, deposits formed on the lower surface of showerhead 32 and the upper surfaces of pumping plate 34 and substrate support 28 would react with the reactive species to form volatile compounds.

The likely deposits to be removed can be better appreciated by referring to FIG. 4 which illustrates the enlarged view A of FIG. 1. FIG. 4 shows that portion of the chamber where pumping plate 34 and substrate support 28 are separated by spacing 38. Because of their relative positions and

11

the chamber design, spacing 38 is at a minimum when pumping plate 34 and substrate support 28 are directly adjacent to each other or in the deposition position as shown in FIGS. 1 and 4. For a substrate support 28 in a position directly adjacent to pumping plate 34 as shown in FIGS. 1 and 4, spacing 38 is on the order of 0.088 and 0.112 inches. Reactive species introduced into chamber region 24 would easily contact and react with deposits 25 formed on the top surfaces of pumping plate 34 and substrate support 28. To a certain extent reactive species introduced within region 24 are hindered from entering region 26 because of spacing 38. As a result, chamber interior region 24 which contains the majority of deposits to be removed is the first region cleaned. During the first cleaning cycle most of the cleaning occurs in the first region 24.

Returning to flow diagram 300 of FIG. 3 and as set forth in block 307, the volatile compounds are removed from the processing chamber. As the reactive fluorine species react with the tantalum pentoxide deposits to form volatile compounds, those compounds are exhausted from the interior regions of chamber 10 via pump 15. This process continues until the deposits formed within processing region 24 have been removed. Typical removal rates for reactive species generated from  $\text{NF}_3$  with the 2:1 inert gas/reactive gas ratio described above is about 1 micron of tantalum pentoxide per minute.

In a specific embodiment of the present invention, the first series of steps 304 through 307 represent providing an advantageous inert gas-cleaning gas mixture to a small volume processing region and a high pressure. For example, the small volume processing region could be the volume of region 24 and the high pressure could be about 2 Torr. One skilled in the art will appreciate that blocks 304, 305, 306 and 307 have been shown and described serially only for clarity in explaining the method of the present invention. In practicing the present invention, one skilled in the art could perform the steps described in blocks 304, 305, 306 and 307 in a different order or nearly simultaneously.

The next step, as set forth in block 308, is to repeat steps 304, 305, 306 and 307 until deposits formed on all interior chamber regions have been removed. This step takes into account restrictions caused by the relative positions of internal chamber components and the relationship between chamber pressure and reactive species. In the first series of steps 304, 305, 306 and 307, deposits were removed primarily from interior chamber region 24. In the second series of steps 304, 305, 306 and 307, reactive species are provided to and deposits are removed from another processing region or, alternatively, a series of processing regions.

In the representative embodiment of chamber 10 illustrated in FIG. 5, substrate support 28 has been repositioned so as to more easily allow remotely activated species into another interior region. Put another way, substrate support 28 is repositioned to increase the fluid communication between processing regions 24 and 26. In this way, reactive species entering region 24 can more easily access region 26 and react with deposits formed therein. In this representative embodiment, the interior region refers to interior regions 24 and 26. Although illustrated with the movement of support 28, other chambers will have other components alter position relative to one another in order to increase fluid communication between first and second or second and subsequent processing regions.

Turning now to FIG. 5 which shows the processing system 5 of FIG. 1 in which steps 301 through 307 above have been conducted. Chamber 10 of FIG. 5 also illustrates

12

the placement of internal components to provide increased fluid communication to an additional processing region. In FIG. 5, resistively heated substrate support 28 in a position below pumping plate 34 which effectively increases spacing 38 which in turn leads to increased fluid communication between region 24 and region 26. As a result, reactive species entering region 24 more easily flow into region 26. For example, if the spacing of substrate support 28 in FIG. 1 is about 400 mils, the spacing in FIG. 5 is about 550 mils. Processing system 5 of FIG. 5 is otherwise similarly configured to processing system 5 of FIG. 1. As such, similar components will be referred to by the same reference numbers.

Referring now to FIG. 6, which is enlarged view A of FIG. 5, the effect of processing steps 301 through 307 as well as the enlarged spacing 38 can be better appreciated. FIGS. 5 and 6 illustrate substrate support 28 in a lowered position below the plane of pumping plate 34. Spacing 38 is considerably larger compared to the spacing 38 represented in when substrate support 28 and pumping plate 34 were in nearly the same horizontal plane as in FIGS. 1 and 4. Increased spacing 38 of FIGS. 5 and 6 allows remotely generated reactive species to be transported into lower chamber interior region 26 to effect the removal of deposits formed therein. Thus, with substrate support 28 in a lowered position, the effective volume of chamber 10 is now the full volume of both internal chamber regions 24 and 26 since spacing 38 is sufficiently large so as not to restrict reactive species introduced into the chamber from each interior region of the chamber. Also shown in FIG. 6 is the removal of deposits 25 from the upper surfaces of both substrate support 28 and pumping plate 34 as a result of the first series of process steps 301 through 307. Additionally, as FIG. 6 illustrates, deposits 25 on the edge and bottom surfaces of substrate support 28 and pumping plate 34 can now be removed since these areas are more readily accessible to reactive species. Step 308 represents the desire to repeat steps 304 through 307 to remove additional deposits from additional processing regions insufficiently cleaned by the first series of steps 304 to 307.

Returning to flow diagram 300 of FIG. 3 and according to block 308, the next step is to repeat blocks 304, 305, 306 and 307 for other interior regions until all deposits are removed or all interior regions are cleaned. It is to be appreciated that the ratio of inert gas to reactive species in the gas mixture provided to the processing region may change during each of the repeated series of steps 304 through 307 or remain at some desired ratio. For example, as described above, the inert gas and the cleaning gas may maintain an advantageous 2:1 ratio. As shown in FIGS. 5 and 6, the interior region of the processing chamber as referred to by step 304 now includes a large volume which includes interior regions 24 and 26.

Next, according to block 305, is adjusting the pressure in chamber 10. Besides increasing spacing 38, it is believed that decreased pressure and the resulting increase in residence time will also help reactive species remove deposits from interior region 26. Accordingly, the pressure within chamber 10 is decreased which spreads reactive species within interior regions 34 and 26. A typical pressure is about 900 mT or approximately half the pressure used in the first step 305.

Next, according to block 306, is to remove deposits by reacting the reactive species with the deposits to form volatile compounds. Here, most of the deposits to be reacted are those remaining on substrate support 28 and pumping plate 34 shown in FIG. 6 as well as other accumulations

which may have occurred within lower deposition region 26. Cleaning continues in region 24 as reactive species react with deposits remaining in that region. As before, the reactive species react with the deposits within the processing region and form volatile compounds.

In a specific embodiment of the present invention, the second series of steps 304 through 307 represents providing an advantageous inert gas-cleaning gas mixture to a larger volume processing region at a lower pressure. For example, where the inert gas-cleaning gas mixture is provided to the combined volumes of regions 24 and 26 at a pressure of about 900 mT. Alternatively, the second series of steps are conducted at a pressure that is about half the pressure used in the first series of steps 304 through 307 in a chamber interior region having a larger volume than the chamber volume cleaned in the first series of steps.

Next, according to block 307, the volatile compounds are removed from the chamber. For example, in chamber 10 volatile compounds would be exhausted from interior regions 24 and 26 via pump 15. If desired, control valve 90 could be aligned to divert or closed in order to prevent the reactive species and inert gas from reaching chamber 10. Diverting or otherwise preventing the reactive species and inert gas from entering chamber 10 allows any residual gases from previous cleaning operations to be exhausted.

Next, according to block 308, steps 304, 305, 306 and 307 are repeated to remove deposits formed in other interior regions. Specifically contemplated is the repetition of steps 304-307 to provide reactive species to each interior chamber region created according to the specific configuration of the chamber to be cleaned by the method of the present invention. Just as substrate support 28 and pumping plate 34 create upper and lower interior regions 24 and 26, other processing chambers will have chamber regions or divisions created by the particular internal components of that chamber.

Although chamber regions 24 and 26 are described with respect to a narrowing between substrate support 28 and a pumping plate 34, these restrictions or obstructions are merely illustrative of similar problems which occur in virtually every type of processing apparatus. Some reactors employ a pumping plate as in chamber 10 while other reactors will have process specific components which also partition, restrict gas flows or otherwise decrease fluid communication between processing regions within the chamber interior. An example includes R.F. enhanced plasma deposition chambers of the type with wafer handling and susceptor lifting mechanisms which, depending on their relative positions, obstruct one another from deposition and cleaning gases. In that type of chamber, processing regions may be created by alternating the handler and lifting mechanisms in order to effectively clean the chamber interior. Another example is an etch chamber which employs a shadow ring to preclude wafer movement during processing. In that chamber, processing regions may be determined by the relative placement of the shadow ring within the chamber. Other examples include tube reactors and other processing systems that utilize track or conveyor systems to move substrates in and out of a processing area. Processing regions in these types of systems could be created by regions which are obstructed by the track system or conveyor system. Other examples of chamber type and process type chamber regions and internal component obstructions within a given chamber will occur to those of ordinary skill in the art and are within the scope of the present invention.

Next, according to block 309, is to deposit a layer of material inside the processing chamber prior to resuming

processing operations. One purpose of this step is to remove residual cleaning gases, reactants and volatile compounds which if allowed to remain in the processing chamber may interfere with the subsequently deposited films. Although purging a chamber with inert gas may be sufficient in some circumstances, some processes achieve improved results by intentionally depositing a layer of film on interior chamber surfaces. The step of seasoning or intentionally depositing a layer of film in a process chamber is of particular importance where Fluorine has been used as a cleaning reactant. Residual fluorine may have detrimental effect on deposited film quality on subsequently processed substrates. Forming a layer of film in a chamber without a substrate present allows residual gases to react, form volatile compounds and be exhausted from the chamber. Additionally, particles remaining within the chamber will become entrapped in the deposited seasoning layer. In either case, the seasoning step ensures that unreacted or residual cleaning gases and by-products are removed from the chamber before resuming processing operations. In a representative embodiment such as a Tantalum deposition chamber, a layer of tantalum pentaoxide may be deposited on substrate support 28 and other interior surfaces of chamber 10 by flowing vaporized TAT-DMAE and an oxidizing gas into the chamber at a temperature of about 475° C. A representative seasoning layer for Ta<sub>2</sub>O<sub>5</sub> about 2500 Å. The particular thickness and composition of a seasoning layer will vary depending on the chamber and type of film deposited.

The final step of the present invention, block 310, is the resumption of processing operations in chamber 10. One such processing operation is the thermal deposition of tantalum pentaoxide by mixing a tantalum precursor with an oxidizing agent at approximately 450° C. Accordingly, a substrate is placed on resistively heated substrate support 28. Heater controller 44 adjusts the power provided heater 29 to maintain the substrate at an appropriate processing temperature of about 450° C. Lift mechanism 42 positions substrate support 28 and the wafer thereupon in chamber 10 relative to showerhead 32 to a spacing of, for example, 400 mils. Gas supplies 46 and 48 of FIG. 1 contain a oxidizing gas such as oxygen or nitrous oxide and a tantalum precursor such as TAT-DMAE or TAETO. Valve and controller mechanism 50 mixes and adjusts the flow rate of the tantalum and oxidizing gases and delivers them to chamber 10. The temperature of the substrate positioned on support 28 is sufficient to form tantalum pentaoxide from the incoming gas stream.

An alternative method of the present invention may also be practiced within a single processing region of a chamber having multiple processing regions (e.g. first and second processing areas 24 and 26 of chamber 10) or in chambers having only a single processing region such as chamber 100 of FIG. 7. The alternative method is practiced by adjusting the cleaning gas/inert gas ratio and the chamber pressure. Turning now to FIG. 7, an embodiment of a chamber having a single processing region can be better appreciated.

FIG. 7 illustrates a representative chamber 100 having a single processing region. Chamber 100 could be an Ultima High Density Plasma (HDP) Chemical Vapor Deposition (CVD) chamber or Ultima HDP CVD™ chamber manufactured by Applied Materials, Inc. of Santa Clara, Calif. Chamber 100 is coupled to plasma generating apparatus 60 and gas supplies 46 and 48. Chamber 100 has a chamber body 105 and a lid 110 that together form a pressure and temperature controlled processing region 107. Substrate support 125 has a top support surface 126 and is disposed within processing region 107. Support arm 130 is coupled to chamber body 105 and supports substrate support 125.

15

Pressure within processing region 107 is provided by turbo pump 140 and roughing pump 150. Throttle valve and gate valve assembly 135 separates processing region 107 from turbo pump 140 and roughing pump 150 and controls the pressure within processing region 107. Plasma apparatus 60 and as well as other similarly numbered elements shown in FIG. 7 are the same as described above with regard to FIGS. 1 and 5. Although, remote plasma apparatus 60 of FIG. 7 is a manual tuner controller 68, an automatic tuner controller could also be used to dissociate the cleaning gas.

Gas supplies 48 and 46 could be any of a variety of process gases used to deposit commercial quality semiconductor films. Gas supplies 46, 48 and valve and controller 50 could be configured to provide precursor material into processing region 107 in order to deposit silicon dioxide, silicon nitride, fluorine doped silicate glass (FSG) or other low dielectric constant films, phosphorus doped silicate glass (PSG) or other premetal dielectric films. Gases from gas supplies 48 and 46 flow through gas supply inlet 52 and then through chamber gas inlets 120. Induction coils 112 provide RF energy to the portion of region 107 above substrate support top surface 126 for deposition processes conducted within chamber 100. The RF energy provided by coils 112 is used only for deposition processes and is not used during the remote cleaning processes of the present invention. In a typical plasma enhanced deposition reactor such as chamber 100 in FIG. 7, deposits would tend to form primarily in the area delineated by coils 112. The influence of coils 112 on deposition within processing region 107 results in the highest concentrations of deposits occurring on the substrate support top surface 126 and along the sides of substrate support 125 and support arm 130. To a lesser extent, deposits also form on the interior surfaces of chamber lid 110 and chamber body 105.

An alternative method of the present invention can be conducted in a single processing region of a chamber, can be better understood by turning to FIG. 8. FIG. 8 is a flow chart of the single processing region method of the present invention.

First, as set forth in block 801 of flow diagram 800 in FIG. 8, after forming deposits within the processing chamber and removing processed substrates from the chamber, initiate a plasma in the remote plasma apparatus. Since a manual tuner controller is used, the plasma is more readily initiated through the use of a plasma initiating gas. Plasma initiation could be accomplished by flowing an inert gas such as Ar through applicator 72 at a rate of about 1000 sccm. After the pressure within chamber 100 rises above 600 mT, magnetron 62 directs microwave energy to the Ar gas flow within applicator 72. Once the plasma is initiated, the cleaning gas is introduced by reducing the flow of the plasma initiating gas while increasing the flow of the cleaning gas. In a representative embodiment using Ar and NF<sub>3</sub>, Ar could be flowed at about 1000 sccm with magnetron 62 producing microwave energy at about 3200 W to initiate a plasma. NF<sub>3</sub> could then be introduced into applicator 72 at about 100 sccm. Shortly thereafter, the flow rate of the cleaning gas is increased while the flow rate of the inert gas is decreased. The result provides a sustained plasma in applicator 72 with the cleaning gas flowing through the applicator and being dissociated in the plasma. In a specific example where only the cleaning gas or NF<sub>3</sub> is desired, the Ar flow rate could be stopped after a stable plasma is formed with the NF<sub>3</sub> flow. Typically in manually tuned systems, Ar is introduced at about 1000 sccm for plasma strike. The NF<sub>3</sub> is introduced and then the Ar flow is adjusted according to the desired Ar/NF<sub>3</sub> ratio. The plasma is now initiated and sustained with

16

only the cleaning gas being introduced and dissociated in applicator 72. It is to be understood that the above process is illustrative of initiating a plasma in a manual tune remote plasma system. An automatically tuned remote plasma system could also be employed to activate or dissociate the cleaning gas directly without first using an inert gas or other plasma initiating gas to initiate a plasma within applicator 72.

Next, as set forth in block 802, is to determine whether to provide cleaning gas dilution. Cleaning gas dilution refers to the addition of an inert gas into the flow of the cleaning gas or reactive species producing gas. As step 802 indicates, the cleaning gas can be provided alone or in combination with an inert gas. If cleaning gas dilution is desired, the next step is set forth in block 811. If cleaning gas dilution is not desired, the next step is set forth in block 803.

In the case where cleaning gas dilution is not desired, proceed to block 803 which provides an adjustment to the cleaning gas flow rate. In this step, the cleaning gas flow rate is adjusted to the desired cleaning step flow rate from the flow rate utilized during plasma initiation. The cleaning gas flow rate could vary depending, for example, upon on the cost of the cleaning gas to be consumed, the power capacity of magnetron 62 and the type of film deposit to be cleaned from the chamber. Recall that the power output of magnetron 62 limits the rate of cleaning gas flow which can be completely or nearly completely dissociated. For example, it is believed that a magnetron 62 rated at 3500 W in a remote plasma apparatus 60 can achieve about 99% dissociation of a 1700 sccm NF<sub>3</sub> gas flow. For a constant magnetron power of 3500 W, gas flows greater than 1700 sccm could result in decreased dissociation percentages. For a given cleaning gas flow rate, lower magnetron power output levels could also result in lower dissociation percentages. For example, an NF<sub>3</sub> flow rate of 300 sccm and a magnetron power of 500 W may produce only about 95% dissociation while an NF<sub>3</sub> flow rate of 1500 sccm and a magnetron power of 3200 W may produce 99% or higher dissociation. After adjusting the cleaning gas flow rate to the desired rate, proceed to block 804.

In the case where cleaning gas dilution is desired, then a mixture of cleaning gas and inert gas is provided to the remote plasma applicator. Cleaning gas dilution could also be accomplished by flowing only the cleaning gas through applicator 72 with the inert gas being introduced downstream of applicator 72. In this case, proceed as set forth in block 811 which provides an adjustment to the cleaning gas flow rate. As stated with regard to block 803, the cleaning gas can be adjusted to the desired rate. After adjusting the cleaning gas flow rate, the next step in cleaning gas dilution is to adjust the inert gas flow rate to the desired rate. The adjustment of the cleaning gas and the inert gas in blocks 811 and 812 is achieved by valve and controllers 80 and 82 of FIG. 7. One of ordinary skill will appreciate that the sequence of adjusting could be reversed so that the inert gas flow is altered before the cleaning gas flow or the gas flows could be adjusted nearly simultaneously. In an illustrative embodiment of the present invention where magnetron 62 delivers 3200 W of microwave energy to applicator 72, the cleaning gas is NF<sub>3</sub> and the inert gas is Ar, representative flow rates for cleaning gas dilution according to the present invention could have a NF<sub>3</sub>/Ar flow ratio of one to one or, preferably, two to one. In a specific embodiment of the present invention, the Ar gas flow rate is 750 sccm, the NF<sub>3</sub> flow rate is 1500 sccm and the microwave energy directed to applicator 72 is 4500 W.

After adjusting the cleaning gas flow rate according to block 803 or adjusting the cleaning gas and the inert gas

17

flows according to blocks 811 and 812, the next step, as set forth in block 804, is to provide reactive species to the processing chamber. Regardless of whether or not cleaning gas dilution is employed, cleaning gas dissociation occurs as the cleaning gas passes through applicator 72 and is exposed to the microwave energy generated by magnetron 62. So long as sufficient microwave energy is provided, cleaning gas provided into applicator 72 will dissociate and form reactive species. For example, if  $\text{NF}_3$  is employed as a cleaning gas, the dissociation that occurs within applicator 72 will produce reactive F, some  $\text{N}_2$ , and trace amounts of NF and  $\text{F}_2$ . Referring again to the illustrative embodiment of chamber 100 in FIG. 7, reactive species exiting applicator 72 flow through supply line 88 past diverter 90 and into chamber supply line 52. From chamber supply line 52, reactive species are provided to processing region 107 via chamber gas inlets 120.

Turning again to FIG. 8, the next step as set forth in block 805, is to adjust the chamber pressure. One method to monitor the pressure within processing region 107 is to employ a capacitance manometer. The desired pressure within processing region 107 is obtained by adjusting the position of throttle valve/gate valve assembly 135 to increase or decrease the conductance between processing region 107 and pumps 140 and 150. Advantageous results have been obtained in pressure ranges between 1 T and 4 T or preferably about 1.8 T and 3 T.

Next, as set forth in block 806, is to react reactive species with and remove chamber deposits. Reactive species entering processing region 107 will combine with the deposits formed in processing region 107 to form volatile compounds that are exhausted from the chamber. In a typical plasma enhanced deposition reactor such as chamber 100 in FIG. 7, deposits would tend to form primarily in the area delineated by coils 112. As a result of the influence of coils 112 on deposition processes conducted within processing region 107, the highest concentrations of deposits are believed to occur on the substrate support top surface 126 and along the sides of substrate support 125 and support arm 130. Deposits also form on the interior surfaces of chamber lid 110 and chamber body 105. Reactive species entering processing region 107 react with the deposits, form volatile compounds and are exhausted from processing region 107.

The next step, as set forth in block 807, is a decision whether to modify gas flow.

In the case where a different inert or cleaning gas flow is desired, return to block 802. At block 802, determine whether cleaning gas dilution will be continued as in the case where dilution is in use, or will be implemented as in the case where non-diluted cleaning gas was employed. Based on adjustments made according to block 803, in the case of no cleaning gas dilution, or according to blocks 811 and 812, in the case of cleaning gas dilution, provide reactive species to the processing chamber (block 804) at the adjusted flow rate. The modified gas flows are employed as before and the chamber pressure can also be adjusted in block 805. Next, the reactive species can react with and remove deposits according to block 806. Once again, and for as many times as necessary, a block 807 determination could be made to return to block 802 and repeat the above steps for different gas flows and chamber pressures.

Once the number of repetitions from block 807 to block 802 are complete or in the case where no gas flow rate adjustment is desired, proceed to the next block which is block 808.

The next step, as set forth in block 808, is to determine whether chamber pressure is to be modified. This step allows

18

the same gas flow to be provided to the chamber while providing different pressures within chamber 100. For example, determining not to modify the gas flow in block 807 followed by deciding to modify chamber pressure in block 808 results in the previously determined compositions of reactive species or reactive species/inert gas mixture being provided to processing region 107 under different pressure conditions. For example, the chamber might be maintained at a constant pressure while providing a variety of different gas flow combinations (e.g., in the case where no pressure adjustment is made in block 805 while opting to adjust gas flows in block 807). Alternatively, various pressures could be employed in chamber 100 while maintaining constant gas flow rates as in the case where no gas flow modification is selected in block 807 but chamber pressure modification is selected at block 808. Also anticipated is a cleaning method which employs multiple pressures and multiple gas flow combinations. As stated above, higher pressures generally result in shorter mean free paths for gases while lower pressures generally result in longer mean free paths for gases. For example, a higher pressure may be used for initial cleaning steps when deposits are greatest and reactions between reactive species and deposits likely. As cleaning progresses and deposits are reduced, lower pressures can be employed to increase residence time thereby increasing the likelihood of reaction between the longer residence time reactive species and the remaining deposits. Also contemplated in the method of the present invention is the advantageous use of both cleaning gas dilution and low chamber pressure to increase the residence time and decrease the recombination of the reactive species thereby improving the chamber cleaning process.

After conducting desired gas flow and pressure combinations provided through responses to blocks 807 and 808, the next step as set forth in block 809 is to season the chamber. As described above with regard to a Tantalum disposition chamber, the quality and reliability of many deposition processes are improved if steps are taken to remove from the processing region residual cleaning gases, reactive species and other volatile compounds created by the cleaning process described above. In the case where the subsequent processing operations include the deposition of silicon nitride, a layer of about 1000 Å silicon nitride is deposited within processing region 107. In the case of silicon dioxide, fluorine doped silicate glass (FSG) or other low dielectric constant films (i.e. films having a dielectric constant below 4.0), phosphorus doped silicate glass (PSG) or other pre-metal dielectric films, a layer of about 1000 Å of silicon dioxide is deposited within processing region 107.

Block 810 of flow diagram 800 sets forth the last step of the present invention which is to resume chamber processing. The cleaning process of block 800 can be repeated as desired depending upon processing requirements. Representative cleaning cycles for typical semiconductor fabrication processes include cleaning the chamber after three to five substrates are processed or after about 3  $\mu\text{m}$  of film has been deposited on substrates processed in chamber 100.

The description above with regard to FIG. 8 sets forth the steps of block diagram 800 serially to provide a more thorough understanding of the present invention. One of ordinary skill in the art will appreciate that many of the steps may be conducted simultaneously or nearly simultaneously. Other minor deviations within flow diagram 800 are also within the scope of the present invention. For example, steps 811 and 812 could be performed in reverse order such that when cleaning gas dilution is desired, the inert gas flow is adjusted before the cleaning gas flow is adjusted.

Additionally, the chamber pressure may be adjusted (blocks 805 and 808) before the determination of whether or not to employ cleaning gas dilution (blocks 802, 811, 812 and 807).

The method of the present invention set forth in flow diagram 800 can be better appreciated by considering the following representative examples. In an embodiment of the present invention, the processing chamber is maintained at a constant pressure while a cleaning gas is provided alone and then in combination with an inert gas in accordance with the present invention. The chamber could have been used for processing operations including the deposition of a low dielectric constant (i.e. a dielectric constant less than 4.0). One such film is fluorine doped silicate glass (FSG). After conducting processing operations which form deposits within the processing chamber and removing the last wafer processed, a 3200 W plasma could be initiated in the remote plasma apparatus. An inert gas such as Argon could be used to initiate the plasma if a manual tuned microwave generator is employed. After initiation, a cleaning gas is provided to the remote plasma apparatus to generate reactive species. In this example,  $\text{NF}_3$  is used and cleaning gas dilution (block 802) is not employed in this portion of the process. Next, according to block 803 the cleaning gas flow rate is adjusted to the desired flow rate. In this example,  $\text{NF}_3$  is provided at about 1500 sccm. As the  $\text{NF}_3$  dissociates and provides reactive species to the processing chamber (block 804) the chamber pressure is maintained at a constant pressure of about 3 Torr (block 805). Reactive species provided by the dissociated cleaning gas react with the deposits formed within the chamber to form volatile compounds that are exhausted from the chamber (block 806). In this example the reactive species are reactive fluorine which removes FSG deposits at between about 1.2  $\mu\text{m}$  to 0.9  $\mu\text{m}$ . In a process where the chamber is cleaned after 3  $\mu\text{m}$  of deposition material is allowed to accumulate, this step lasts approximately 75 to 100 seconds.

The next step in this example is to modify gas flow in response to block 807 and employ cleaning gas dilution in response to block 802. In response to blocks 811 and 812, the cleaning gas and inert gas flows are adjusted and maintained at a level such that complete or nearly complete dissociation occurs in applicator 72. In this example, the cleaning gas is  $\text{NF}_3$  and inert gas is Argon and they are provided in a 1:1 ratio, where  $\text{NF}_3$  could be adjusted to 750 sccm while Ar is adjusted to 750 sccm. Alternatively, advantageous results may be obtained by providing a 2:1 ratio between the cleaning gas and the inert gas. Again using  $\text{NF}_3$  and Ar as examples, the flows could be adjusted to provide 1000 sccm  $\text{NF}_3$  while providing 500 sccm Ar. In both the 1:1 and 2:1 ratio examples where the cleaning gas is  $\text{NF}_3$  or other gas with a similar dissociation energy requirement, the total flow rate through applicator 72 is 1500 sccm which if employed with a 3500 W output from magnetron 62 is believed to produce complete or nearly complete (i.e. about 99%) dissociation of the cleaning gas.

As the cleaning gas, in this example  $\text{NF}_3$ , dissociates and provides reactive species to the processing chamber (block 804) the chamber pressure is maintained at a constant pressure of about 3 Torr (block 805). Reactive species provided by the dissociated cleaning gas react with the deposits formed within the chamber to form volatile compounds that are exhausted from the chamber (block 806).

Next, after the removal of deposits conducted in accordance with block 806 is complete, then the cleaning gas and inert gas flows could be modified according to blocks 807 and 802 to provide another combination of cleaning gas and

inert gas or to provide cleaning gas alone. According to this specific example, gas flow and chamber pressure modifications according to blocks 807 and 808 are not desired. Instead, in accordance with block 809, the chamber is seasoned by depositing a layer of film before resuming processing operations. For example, in a processing apparatus used to deposit FSG a layer of about 1000 Å of  $\text{SiO}_2$  may be deposited. In this specific example, the next step in according to block 810 is to resume FSG deposition operations in the processing chamber.

In another specific embodiment of the present invention, the cleaning method would employ at least two different pressures along with cleaning gas alone and cleaning gas diluted by an inert gas. Initially, a high pressure is used when the amount of deposits is greatest followed by a low pressure clean when the amount of deposits is reduced and dispersed within the chamber. The chamber could have been used for processing operations such as the deposition of a premetallized dielectric. One such film is phosphorus doped silicon glass (PSG). After conducting processing operations which form deposits within the processing chamber and removing the last wafer processed, a 3200 W plasma could be initiated in the remote plasma apparatus. As described above, an inert gas such as Argon could be used to initiate the plasma if a manual tuned microwave generator is employed. After initiation, a cleaning gas is provided to the remote plasma apparatus to generate reactive species. In this example,  $\text{NF}_3$  is used and cleaning gas dilution (block 802) is not employed in this portion of the process. Next, according to block 803 the cleaning gas flow rate is adjusted to the desired flow rate. In this example,  $\text{NF}_3$  is provided at about 1500 sccm. As the  $\text{NF}_3$  dissociates and provides reactive species to the processing chamber (block 804) the chamber pressure is maintained at a constant pressure of about 3 Torr (block 805). Reactive species provided by the dissociated cleaning gas react with the deposits formed within the chamber to form volatile compounds that are exhausted from the chamber (block 806).

The next step in this representative remote clean process of the present invention is to modify the gas flow in response to block 807 and employ cleaning gas dilution in response to block 802. In response to blocks 811 and 812, the cleaning gas and inert gas flows are adjusted. In this example where the cleaning gas is  $\text{NF}_3$  and inert gas is Argon, the gases could be provided in a 1:1 ratio such as where  $\text{NF}_3$  is 750 sccm and Ar is 750 sccm. Alternatively, better cleaning uniformity may be obtained by providing a 2:1 ratio between the cleaning gas and the inert gas as in where the gas flows are adjusted to provide 1000 sccm  $\text{NF}_3$  and 500 sccm Ar or, preferably, 1500 sccm  $\text{NF}_3$  and 750 sccm Ar. As in the previous example, total flow through applicator 72 and microwave power are maintained at a level where complete or nearly complete dissociation of the cleaning gas is achieved.

As the cleaning gas inert gas mixture dissociates and provides reactive species to the processing chamber (block 804) the chamber pressure is decreased to a pressure of about 1.8 Torr (block 805). Reactive species have a longer residence time at the lower pressure thereby increasing the likelihood that they will react with the remaining deposits formed within the chamber to form volatile compounds that are exhausted from the chamber (block 806).

After the removal of deposits conducted in accordance with block 806 is complete, the chamber is seasoned by depositing a layer of film in accordance with block 809 before resuming processing operations. For example, in a processing apparatus used to deposit PSG a layer of about



1000 Å of SiO<sub>2</sub> may be deposited in processing region 107 while no substrate is present within region 107. Next according to block 810, resume the deposition of PSG films on substrates in the processing chamber.

In addition to the above specific embodiments, it is anticipated that several gas flow rates and chamber pressures may be employed and modified through successive iterations of the steps in block diagram 800. It is also anticipated that the methods of block diagram 800 may be employed with the methods of block diagram 300. One result illustrative of such a combined method would be the employment of the gas mixing and chamber pressure adjustments of block diagram 800 into the multiple interior regions formed within a processing reactor 10.

Referring now to FIGS. 9, 10 and 11, the advantageous cleaning rate and cleaning uniformity achieved by a method of the present invention set forth in FIG. 3 can be better appreciated. The results illustrated in FIGS. 9, 10 and 11 were obtained by measuring the initial thickness and uniformity of a SiO<sub>2</sub> film deposited on several 200 mm wafers then exposing those wafers to different process conditions within a chamber 10 to determine the effect of the different process conditions on cleaning rate and uniformity. After exposure to a particular cleaning process environment, film thickness and uniformity was again measured and compared to the original thickness and uniformity. Each graph represents a different variable such as various Ar flow rates in FIG. 9, various NF<sub>3</sub> flow rates in FIG. 10 and various chamber pressures in FIG. 11.

FIG. 9 represents the effect of increased Argon flow rate on clean rate and uniformity while chamber pressure and NF<sub>3</sub> flow are constant. While maintaining a chamber pressure of 2 Torr and a NF<sub>3</sub> flow rate of 200 sccm, Ar flow was varied from 0 to 1000 sccm. The flow rate of 400 sccm provided the highest clean rate of about 7500 Å/min and the lowest uniformity of about 11%. As Ar flow rate increased above 400 sccm or as the NF<sub>3</sub> flow is further diluted by the higher Ar flow, the cleaning rate decreased to between about 4100 and 5800 Å/min while the uniformity increased to as much as 35%. As the Ar flow decreased below 400 sccm the cleaning rate decreased below 7500 Å/min to as low as 6000 Å/min while the clean uniformity increased to between 12% to 25%.

FIG. 10 represents the effect of increased NF<sub>3</sub> flow on cleaning rate and uniformity. While maintaining chamber pressure at 2 Torr and Ar flow rate at 400 sccm, NF<sub>3</sub> flow rate was increased from 0 sccm to 400 sccm. At 200 sccm of NF<sub>3</sub>, the cleaning rate was about 7500 Å/min with a clean uniformity of about 10%. Increasing NF<sub>3</sub> flow above 200 sccm led to a decreased clean rate of about 6000 Å/min and an increased clean uniformity of about 15%. Decreasing the NF<sub>3</sub> flow rate below 200 sccm decreased the cleaning rate to about 3000 Å/min while increasing the clean uniformity to between 20% to 30%.

FIG. 11 represents the effect of chamber pressure on cleaning rate and clean uniformity for constant Ar and NF<sub>3</sub> flow rates. At 2 Torr chamber pressure the clean uniformity was about 10% while the clean rate was about 7500 Å/min. At pressures below 2 Torr the clean uniformity is only moderately increased however the cleaning rate decreases to about 300 Å/min. At pressures above 2 Torr, the uniformity is above 20% while the cleaning rate is only about 3000 Å/min. A higher cleaning rate is indicative of a more rapid clean and a low cleaning uniformity indicates that the cleaning radicals are more evenly applied throughout the chamber interior thereby reducing the likelihood that some

chamber components may be overcleaned and damaged. Thus, a review of the results obtained and illustrated in FIGS. 9, 10 and 11, an advantageous clean having the highest cleaning rate and lowest uniformity could be achieved using the methods of the present invention in a chamber 10 at a pressure of 2 Torr and Ar/NF<sub>3</sub> mixture activated in applicator 72 and provided to the chamber in a 2:1 ratio or the specific embodiment of 400 sccm Ar and 200 sccm of NF<sub>3</sub> and a microwave power of 1400 Watts.

FIG. 12 represents alternative results obtained in a test conducted in a chamber similar to chamber 100 of FIG. 7. In this test a silicon dioxide film was deposited on a 300 mm wafer and the initial thickness and uniformity of the film was measured. The wafer was then placed in a chamber 100 and exposed to cleaning process conditions similar to the cleaning method set forth in FIG. 8. After conducting the cleaning process, the wafer was removed from the chamber and the thickness and uniformity of the film was again measured. These post cleaning measurements are illustrated in FIG. 12. The method of FIG. 8 was conducted in a chamber 100 with a 1:2 Ar/NF<sub>3</sub> ratio, in this embodiment a 750 sccm Ar flow and 1500 sccm NF<sub>3</sub> flow were used, with a microwave power of 4500 Watts and a chamber pressure of 3 Torr. This specific embodiment of the method of FIG. 8 achieved a cleaning uniformity of 4.34% and a cleaning rate of 2000 Å/min.

While specific embodiments of the invention have been shown and described, further modifications and improvements will occur to those skilled in the art. It is desired that it be understood, therefore, that the invention is not limited to the particular form shown and it is intended in the appended claims which follow to cover all modifications which do not depart from the spirit and scope of the invention.

We claim:

1. A method of cleaning from a processing chamber deposits formed on interior surfaces of the processing chamber wherein said processing chamber interior surfaces include a first region and a second region said second region being different from said first region, said method comprising the steps of:

- (a) dissociating a gas mixture outside said processing chamber to form reactive species, said gas mixture comprising an inert gas and a cleaning gas;
- (b) providing said reactive species to said processing chamber;
- (c) reacting said reactive species with said deposits in said processing chamber first region;
- (d) forming volatile compounds from said deposits formed in said processing chamber first region;
- (e) removing from said processing chamber said volatile compounds formed from deposits formed in said processing chamber first region;
- (f) increasing the fluid communication between said processing chamber first and second regions;
- (g) reacting said reactive species with said deposits in said processing chamber second region;
- (h) forming volatile compounds from said deposits formed in said processing chamber second region;
- (i) removing from said processing chamber said volatile compounds formed from deposits formed in said processing chamber second region.

2. The method according to claim 1 wherein the ratio of said inert gas to said cleaning gas is about 2 to 1.

3. The method according to claim 1 wherein said step of dissociating a gas mixture outside said processing chamber

to form reactive species is conducted in a microwave powered remote plasma apparatus.

4. The method of claim 1 wherein said step of reacting said reactive species with deposits formed in said processing chamber first region is performed at a first pressure and said step of reacting said reactive species with deposits formed in said processing chamber second region is performed at a second pressure wherein said second pressure is different from said first pressure.

5. The method of claim 2 wherein said first gas is an inert gas and said second gas is a halogenated gas.

6. The method of claim 5 wherein said halogenated gas is  $\text{NF}_3$ .

7. The method according to claim 3 wherein said microwave power causes more than 99% dissociation of said cleaning gas within said gas mixture.

8. The method of claim 4 wherein said first pressure is greater than said second pressure.

9. The method of claim 4 wherein said first pressure is about twice the second pressure.

10. The method of claim 4 wherein said first pressure is about 2 Torr.

11. A method of removing deposits formed in a processing chamber as a result of deposition operations performed on a substrate disposed within the processing chamber, the method comprising the steps of:

- (a) activating a cleaning gas in a remote chamber separate from said processing chamber to form reactive species from said cleaning gas;
- (b) providing an inert gas which mixes with said reactive species to form a gas mixture comprising reactive species;
- (c) providing said gas mixture to said processing chamber while maintaining said processing chamber at a first pressure;
- (d) while maintaining said processing chamber at said first pressure, reacting said reactive species with said deposits to form volatile compounds and thereafter removing from said processing chamber said volatile compounds formed at said first pressure;
- (e) providing said gas mixture comprising reactive species to said processing chamber while maintaining said processing chamber at a second pressure that is different from said first pressure;
- (f) while maintaining said processing chamber at said second pressure, reacting said reactive species with said deposits to form volatile compounds and thereafter removing from said processing chamber said volatile compounds formed at said second pressure; and
- (g) conducting processing operations in said processing chamber to form a film on interior surfaces of said processing chamber without a substrate disposed within said chamber.

12. A method according to claim 11 wherein said second pressure is lower than said first pressure.

13. A method according to claim 11 wherein said second pressure is about half of said first pressure.

14. A method according to claim 11 wherein the step of providing an inert gas which mixes with said reactive species to form a gas mixture comprising reactive species further comprises an inert gas flow rate that is twice the flow rate of the cleaning gas used to form reactive species.

15. A method according to claim 11 further comprising the step of providing said gas mixture comprising reactive species to a first processing region of said processing chamber while maintaining said first pressure and providing said gas mixture comprising reactive species to a second processing region different from said first processing region while maintaining said second pressure in said processing chamber.

16. A method of removing deposits comprising Tantalum formed on interior surfaces of a processing chamber as a result of substrate processing operations conducted to deposit a film comprising Tantalum on a substrate, said processing chamber comprising a first processing region and a second processing region different from said first processing region, the method comprising the steps of:

- (a) initiating a plasma in a remote chamber outside of said processing chamber;
- (b) activating said cleaning gas with said plasma to generate reactive species from said cleaning gas;
- (c) providing an inert gas that mixes with said reactive species forming a gas mixture comprising inert gas and reactive species;
- (d) providing said gas mixture to the first processing region within said processing chamber;
- (e) while maintaining said processing chamber at a first pressure, reacting said reactive species with said film comprising Tantalum within said first processing region to form volatile compounds;
- (f) removing said volatile compounds formed within said first processing region from said processing chamber;
- (g) increasing the fluid communication between said first and said second processing regions;
- (h) providing said gas mixture to a second processing region within said processing chamber;
- (i) while maintaining said processing chamber at a second pressure, reacting said reactive species with said film comprising Tantalum within said second processing region to form volatile compounds; and
- (j) removing said volatile compounds formed within said second processing region from said processing chamber.

17. The method according to claim 16 comprising the further step following step (j) of conducting processing operations in said processing chamber without a substrate present in said chamber to form a film comprising Tantalum on interior surfaces of said processing chamber wherein said processing operations are conducted after removing from said processing chamber said volatile compounds formed from said first and second processing regions.

18. The method according to claim 16 wherein said cleaning gas is a halogen.

19. The method according to claim 16 wherein said cleaning gas comprises fluorine.

20. The method according to claim 16 wherein said cleaning gas is  $\text{NF}_3$ .

21. The method according to claim 16 wherein said inert gas is selected from the group consisting of Ar, Xe, Ne, He, and  $\text{N}_2$ .



US 20020033183A1

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2002/0033183 A1  
SUN et al. (43) Pub. Date: Mar. 21, 2002(54) METHOD AND APPARATUS FOR  
ENHANCED CHAMBER CLEANING

## Publication Classification

(76) Inventors: SHENG SUN, FREMONT, CA (US);  
QUANYUAN SHANG, SARATOGA,  
CA (US); SANJAY YADAV,  
REDWOOD CITY, CA (US);  
WILLIAM R. HARSHBARGER,  
SAN JOSE, CA (US); KAM S. LAW,  
UNION CITY, CA (US)(51) Int. Cl.<sup>7</sup> ..... B08B 7/04; B08B 7/00; B08B 9/00  
(52) U.S. Cl. .... 134/1.1; 134/1; 134/1.2; 134/1.3;  
134/19; 134/22.1; 134/22.18;  
156/345; 438/905; 134/902

## (57) ABSTRACT

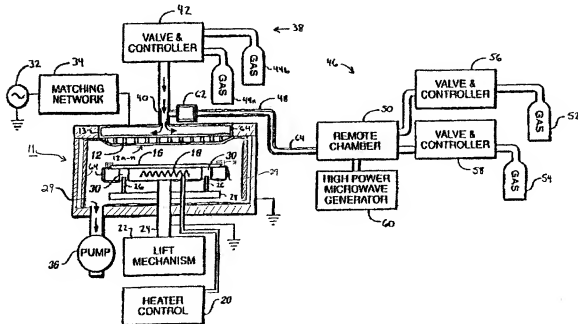
Correspondence Address:  
PATENT COUNSEL MS 2061  
LEGAL AFFAIRS DEPARTMENT  
APPLIED MATERIALS INC  
3050 BOWERS AVENUE  
SANTA CLARA, CA 95052

A system for processing substrates within a chamber and for cleaning accumulated material from chamber components is provided. The system includes a reactive species generator adapted to generate a reactive gas species for chemically etching accumulated material from chamber components, and a processing chamber having at least one fluoropolymer coated component which is exposed to the reactive species. Preferably to have the greatest impact on chamber cleaning efficiency, the fluoropolymer coated component(s) are large components such as a gas distribution plate or a backing plate, and/or a plurality of smaller components (e.g., a shadow frame, chamber wall liners, a susceptor, a gas conductance line) so as to constitute a large percentage of the surface area exposed to the reactive species. Most preferably all surfaces which the reactive species contacts are coated with fluoropolymer.

(\*) Notice: This is a publication of a continued prosecution application (CPA) filed under 37 CFR 1.53(d).

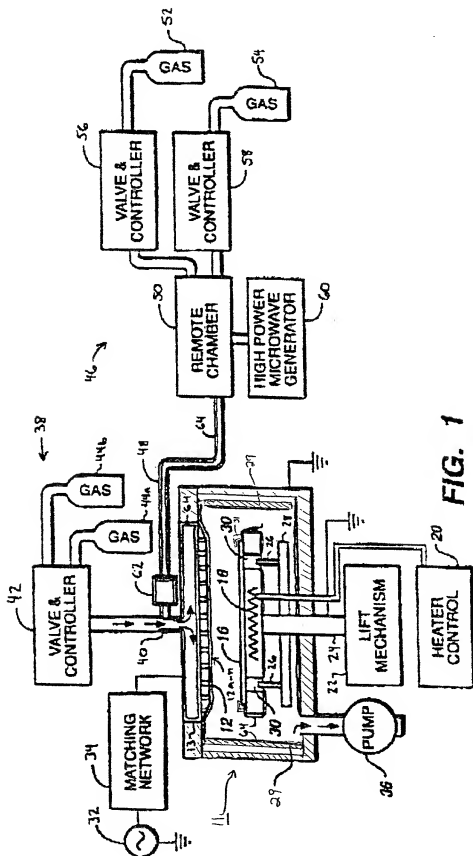
(21) Appl. No.: 09/322,893

(22) Filed: May 29, 1999



## APPENDIX B

Appl. No.: 10/759,953



## METHOD AND APPARATUS FOR ENHANCED CHAMBER CLEANING

### FIELD OF THE INVENTION

[0001] The present invention relates to an improved method and apparatus for enhancing chamber cleaning rates. More specifically, the present invention relates to a method and apparatus for enhancing the effective etch rate of a reactive chemical species which etches accumulated materials from process chamber components.

### BACKGROUND OF THE INVENTION

[0002] The manufacture of liquid crystal displays, flat panel displays, thin film transistors and other semiconductor devices occurs within a plurality of chambers, each of which is designed to perform a specific process on the substrate. Many of these processes can result in an accumulation of material (e.g., material deposited on the substrate in layers, such as by chemical vapor deposition, physical vapor deposition, thermal evaporation, material etched from substrate surfaces, and the like) on chamber surfaces. Such accumulated material can crumble from the chamber surfaces and contaminate the sensitive devices being processed therein. Accordingly, process chambers must be cleaned of accumulated materials frequently (e.g., every 1-6 substrates).

[0003] To clean chamber surfaces, an in-situ dry cleaning process is preferred. In an in-situ dry cleaning process one or more gases are dissociated to form one or more reactive gas species (e.g., fluorine ions, radicals). The reactive species clean chamber surfaces by forming volatile compounds with the material accumulated on those surfaces. Unfortunately, as described further below, such chamber cleaning processes conventionally require considerable time and consume considerable amounts of cleaning gases, and thus undesirably increase the cost per substrate processed within a processing chamber. Further, large cleaning rate variations often are observed between processing chambers cleaned by identical cleaning processes. Accordingly, there is a need for an improved method and apparatus for etching accumulated material from chamber surfaces.

### SUMMARY OF THE INVENTION

[0004] The present inventors have discovered that chamber cleaning rates may be increased by as much as 20-100% when chamber surfaces exposed to reactive cleaning gas species are coated with a fluoropolymer (e.g., polytetrafluoroethylene (PTFE), a tetrafluoroethylene and hexafluoropropylene copolymer (FEP), a copolymer of tetrafluoroethylene and perfluoropropylvinyl ether (PFA)). The present invention therefore comprises a system for processing substrates within a chamber and for cleaning accumulated material from chamber components. The system includes a reactive species generator adapted to generate a reactive gas species for chemically etching accumulated material from chamber components, and a processing chamber having at least one fluoropolymer coated component which is exposed to the reactive species. Preferably to have the greatest impact on chamber cleaning efficiency, the fluoropolymer coated component(s) include large components such as a gas distribution plate or a backing plate, and/or a plurality of smaller components (e.g., the chamber's shadow frame, wall liners, susceptor, gas conductance line, etc.) so as to constitute a

large percentage of the surface area exposed to the reactive species. Most preferably all surfaces which the reactive species contacts are coated with a fluoropolymer.

[0005] By coating exposed chamber components with PTFE, FEP or PFA, not only have cleaning rate enhancements been observed, cleaning rate variations between processing chambers can be virtually eliminated, process chamber throughput increased significantly and the amount of precursor gas required for cleaning reduced. Because of the high costs associated with precursor gases such as  $\text{NF}_3$ , both monetarily and environmentally (e.g., global warming), any reduction in precursor gas consumption is beneficial.

[0006] Other objects, features and advantages of the present invention will become more fully apparent from the following detailed description of the preferred embodiments, the appended claims and the accompanying drawings.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 is a side elevational view of a processing system configured in accordance with the present invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0008] FIG. 1 is a side elevational view of a processing system 10 configured in accordance with the present invention. Any suitable processing system may be modified as described herein such as a model AKT-1600 PECVD System manufactured by Applied Kamatsu Technology and described in U.S. Pat. No. 5,788,778, which is hereby incorporated by reference herein in its entirety, the GIGA-FILL™ processing system manufactured by Applied Materials, Inc. and described in U.S. Pat. No. 5,812,403, which is hereby incorporated by reference herein in its entirety, thermal deposition chambers and the like. For convenience an AKT-1600 PECVD System configured in accordance with the present invention is shown in FIG. 1. The AKT-1600 PECVD System is designed for fabricating active-matrix liquid crystal displays and may be used to deposit amorphous silicon, silicon dioxide, silicon oxynitrides and silicon nitride as is known in the art.

[0009] With reference to FIG. 1, the processing system 10 comprises a deposition chamber 11 having a gas distribution plate 12 having apertures 12a-u and a backing plate 13 adapted to deliver process gases and cleaning gases into the deposition chamber 11, and a susceptor 14 for supporting a substrate 16 to be processed within the deposition chamber 11. The susceptor 14 includes a heater element 18 (e.g., a resistive heater) coupled to a heater control 20 for elevating the temperature of the substrate 16 to a processing temperature and for maintaining the substrate 16 at the processing temperature during processing. A lift mechanism 22 is coupled to the susceptor 14 via a lift member 24 to allow the substrate 16 to be lifted from the susceptor 14. Specifically, a plurality of lift pins 26 (fixedly held by a lift pin holder 28) penetrate the susceptor 14 (via a plurality of lift pin apertures 30) so as to contact and lift the substrate 16 from the susceptor 14 when the susceptor 14 is lowered by the lift mechanism 22. The deposition chamber 11 further comprises a chamber wall liner 29 which blocks material from accumulating on the chamber wall and which can be removed and cleaned, and a shadow frame 31 which over-

hangs the substrate's edge and thereby prevents material from depositing or accumulating on the wafer's edge.

[0010] In addition to their above described functions, the gas distribution plate 12 and the susceptor 14 also serve as parallel plate upper and lower electrodes, respectively, for generating a plasma within the deposition chamber 11. For example, the susceptor 14 may be grounded and the gas distribution plate 12 coupled to an RF generator 32 via a matching network 34. An RF plasma thereby may be generated between the gas distribution plate 12 and the susceptor 14 through application of RF power supplied thereto by the RF generator 32 via the matching network 34. A vacuum pump 36 is coupled to the deposition chamber 11 for evacuating/pumping the same before, during or after processing as required.

[0011] The processing system 10 further comprises a first gas supply system 38 coupled to an inlet 40 of the deposition chamber 11 for supplying process gases thereto through the backing plate 13 and the gas distribution plate 12. The first gas supply system 38 comprises a valve controller system 42 (e.g., computer controlled mass flow controllers, flow meters, etc.) coupled to the inlet 40 of the deposition chamber 11, and a plurality of process gas sources 44a, 44b coupled to the valve controller system 42. The valve controller system 42 regulates the flow of process gases to the deposition chamber 11. The specific process gases employed depend on the materials being deposited within the deposition chamber 11.

[0012] In addition to the first gas supply system 38, the processing system 10 comprises a second gas supply system 46 coupled to the inlet 40 of the deposition chamber 11 (via a gas conductance line 48) for supplying cleaning gases thereto during cleaning of the deposition chamber 11 (e.g., to remove accumulated material from the various interior surfaces of the chamber 11). The second gas supply system 46 comprises a remote plasma chamber 50 coupled to the gas conductance line 48 and a precursor gas source 52 and a minor carrier gas source 54 coupled to the remote plasma chamber 50 via a valve controller system 56 and a valve controller system 58, respectively. Typical precursor cleaning gases include  $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ , etc., as are well known in the art. The minor carrier gas, if employed, may comprise any non-reactive gas compatible with the cleaning process being employed (e.g., argon, helium, hydrogen, nitrogen, oxygen, etc.). The precursor and minor carrier gas sources 52, 54 may comprise a single gas source if desired.

[0013] A high power microwave generator 60 supplies microwave power to the remote plasma chamber 50 to activate the precursor gas within the remote activation chamber (as described below). A flow restrictor 62 preferably is placed along the gas conductance line 48 to allow a pressure differential to be maintained between the remote plasma chamber 50 and the deposition chamber 11.

[0014] During cleaning of the deposition chamber 11, a precursor gas is delivered to the remote plasma chamber 50 from the precursor gas source 52. The flow rate of the precursor gas is set by the valve controller system 56. The high power microwave generator 60 delivers microwave power to the remote plasma chamber 50 and activates the precursor gas to form one or more reactive species (e.g., fluorine radicals) which travel to the deposition chamber 11

through the gas conductance line 48. The one or more reactive species then travel through the inlet 40, through the backing plate 13, through the gas distribution plate 12 and into the deposition chamber 11. A minor carrier gas may be supplied to the remote plasma chamber 50 from the minor carrier gas source 54 to aid in transport of the one or more reactive species to the chamber 11 and/or to assist in chamber cleaning or plasma initiation/stabilization within the deposition chamber 11 if an RF plasma is employed during chamber cleaning.

[0015] Exemplary cleaning process parameters for the deposition chamber 11 when an  $\text{NF}_3$  precursor cleaning gas is employed include a precursor gas flow rate of about 2 liters per minute and a deposition chamber pressure of about 0.5 Torr. A microwave power of 3-12 kW, preferably 5 kW, is supplied to the remote plasma chamber 50 by the high power microwave generator 60 to activate the  $\text{NF}_3$  precursor gas. Preferably the remote plasma chamber 50 is held at a pressure of at least 4.5 Torr and preferably about 6 Torr. Other cleaning process parameter ranges/chemistries are described in previously incorporated U.S. Pat. No. 5,788, 778.

[0016] As previously described, common problems with conventional cleaning processes include low cleaning rates and large variations in cleaning rates between process chambers. The present inventors have discovered that cleaning rates and cleaning rate variations between chambers are dependent on the internal chamber surface condition, and that all internal surfaces between a remote plasma source (e.g., remote plasma chamber 50) and a chamber (e.g., deposition chamber 11) ("downstream surfaces") affect cleaning rates. Specifically, a surface controlled deactivation process is believed to cause reactive species employed during cleaning (e.g., active etchant species such as F radicals) to combine to form non-reactive species (e.g.,  $\text{F}_2$  in the case of F radicals) which do not assist in chamber cleaning. This surface controlled deactivation process appears to occur at many material surfaces including both bare and anodized aluminum surfaces.

[0017] The present inventors have found that by coating one or more downstream components with PTFE, FEP or PFA, known generally as fluoropolymers, significantly higher cleaning rates are achieved and cleaning rate variations between chambers are virtually eliminated. Components found to have the most significant effect on cleaning performance include a chamber's gas distribution plate and backing plate. Components found to have a slight effect on cleaning performance include a chamber's shadow frame, wall liners, susceptor and gas conductance line. Components found to have little effect on cleaning performance include a chamber's microwave power supply, magnetron and microwave applicator. In order to affect an improvement in chamber cleaning rates, a certain percentage of the chamber components should be coated with a fluoropolymer. Although this percentage may vary, higher percentages are preferred to achieve faster cleaning rates, with 100% coating of exposed surfaces being most preferred. Note that an increase in cleaning rate (e.g., up to 15%) also can be achieved by using an RF plasma within a processing chamber in conjunction with a remote plasma source, i.e., by powering electrode 12 to form the radicalized gases entering from the remote plasma source, or secondarily introducing cleaning gases into a plasma. However, applied RF power

should be limited to avoid damage to processing chamber components due to ion bombardment.

[0018] With reference to the processing system 11 of FIG. 1, to affect increased cleaning rate and reduced cleaning rate variations between the deposition chamber 11 and other deposition chambers (not shown), one or more downstream components of the processing system 11 are coated with a polytetrafluoroethylene (PTFE), a tetrafluoroethylene and hexafluoropropylene copolymer (FEP), or a copolymer of tetrafluoroethylene and perfluoropolyvinyl ether coating ("fluoropolymer coating 64"). As shown in FIG. 1, the interior surfaces of the deposition chamber 11, the gas distribution plate 12 the backing plate 13, the susceptor 14, the inlet 40, the gas conductance line 48, the chamber wall liner 29 and the shadow frame 31 are coated with the protective coating 64. Fewer components may be coated with the fluoropolymer coating 64 if desired.

[0019] With respect to the PECVD deposition chamber 11 of FIG. 1, the fluoropolymer coating 64 significantly increases the cleaning rate and significantly reduces chamber-to-chamber cleaning rate variations while neither producing process drift nor changes in the properties of PECVD films deposited within the deposition chamber 11. The fluoropolymer coating 64 is believed to cover surface adsorption sites at which the surface controlled deactivation process is believed to occur (e.g., maintaining a high and a uniform F radical concentration) and is also believed to reduce the amount of material deposited on component surfaces of the deposition chamber 11 during processing therein (e.g., reducing the amount of material that must be cleaned from component surfaces and the time required for material removal during cleaning).

[0020] The inventive fluoropolymer coating may be applied either in-situ or ex-situ. For in-situ application of PTFE coatings, a precursor gas such as  $\text{CHF}_3$  may be employed to coat process chamber components using either a microwave or RF plasma. For example, within the processing system 10, a  $\text{CHF}_3$  precursor gas source 52 may feed  $\text{CHF}_3$  to the remote plasma chamber 50 wherein microwave power applied via the high power microwave generator 60 dissociates the  $\text{CHF}_3$  into  $\text{CF}_2$  and HF. The  $\text{CF}_2$  and HF travel to the deposition chamber 11, and, en route, the  $\text{CF}_2$  forms a fluoropolymer coating on the gas conductance line 48, the flow restrictor 59, the inlet 40, the backing plate 13, the gas distribution plate 12, the susceptor 14 and the interior surfaces of the deposition chamber 11. Alternatively,  $\text{CHF}_3$  (and, if desired,  $\text{CF}_2$  from the remote plasma chamber 50) may be flowed into the deposition chamber 11 while an RF plasma is generated within the deposition chamber 11 via the RF generator 32. As with the microwave plasma of the remote plasma chamber 50, the RF plasma within the deposition chamber 11 will dissociate  $\text{CHF}_3$  into  $\text{CF}_2$  which in turn will coat chamber components with a fluoropolymer coating. Thereafter, the chamber 11 may be heated (e.g., via the heater control 20 and the resistive heating element 18 or via any conventional heating mechanism capable of heating the entire chamber to the desired temperature) so as to melt/reflow the fluoropolymer coating. Preferably a heater temperature of about 500-800° F. is employed. In this manner, a uniform fluoropolymer coating, preferably about 0.5-10  $\mu\text{m}$  in thickness, is formed on the chamber components.

[0021] For ex-situ application of protective coatings, chamber components such as the gas distribution plate 12 and the backing plate 13 preferably are uniformly coated with a thin layer (e.g., about 0.5 to 10 microns) of a PTFE, a FEP- or a PFA-contained in a solution or suspension fluid such as water, isopropyl alcohol, etc. After a few minutes of air drying or after an oven bake at 500-800° F. heater temperature, the chamber components may be reinstalled within the processing chamber. Care should be taken to prevent clogging of the small gas injection holes of the gas distribution plate due to capillary effect.

[0022] It should be noted that the inventive protective coating described herein differs from fluoropolymers which undesirably accumulate over time on chamber surfaces as a result of fluoropolymer deposition on a underlying substrate, or which are formed as a byproduct of certain CVD processes (i.e., are not continuously formed), in that such undesirably accumulated material is characteristically non-uniform, often exhibiting both areas of thick accumulation which can crumble from chamber surfaces, and areas where no material accumulates. Accordingly, such undesirable byproduct and deposited material accumulation must be cleaned from chamber surfaces. However, these undesirable fluoropolymer accumulations do not react with reactive fluorine gas species and therefore must be cleaned by other, less efficient means.

[0023] By coating downstream chamber components with PTFE, FEP or PFA, cleaning rate enhancements of as much as 100% have been observed, and cleaning rate variations between processing chambers have been virtually eliminated. Accordingly, process chamber throughput increases significantly with use of the present invention, and the amount of precursor gas required for cleaning is reduced. Because of the high costs associated with precursor gases such as  $\text{NF}_3$ , both monetarily (e.g.  $\text{NF}_3$  presently costs \$100/lb) and environmentally (e.g.,  $\text{NF}_3$  is a "global warming" gas), reduction in precursor gas consumption is extremely beneficial. Moreover, fluoropolymers are non-brittle, inexpensive and easy to apply, unlike coatings (e.g.,  $\text{AlF}_3$ ) which conventionally have been applied to prevent corrosion of chamber surfaces or to prevent accumulated material from crumbling therefrom.

[0024] The foregoing description discloses only the preferred embodiments of the invention, modifications of the above disclosed apparatus and method which fall within the scope of the invention will be readily apparent to those of ordinary skill in the art. For instance, while the present invention has been described with reference to a PECVD chamber, it will be understood that the invention has applicability to a wide variety of process chambers including thermal deposition chambers. Additionally, cleaning processes employing reactive species (e.g., reactive species generated by an RF plasma within a process chamber, or remote plasma source generated reactive species etc.) may be improved by employing the fluoropolymer coatings described herein. Finally, although any fluoropolymer is believed to enhance cleaning when applied as described herein, the fluoropolymers PTFE, FEP and PFA have been found to significantly enhance cleaning and are preferred.

[0025] Accordingly, while the present invention has been disclosed in connection with the preferred embodiments

thereof, it should be understood that other embodiments may fall within the spirit and scope of the invention, as defined by the following claims.

The invention claimed is:

1. A gas distribution plate adapted to distribute gas as the gas flows into a processing chamber, the gas distribution plate comprising:

a base having a plurality of apertures formed therein; and  
a continuously formed fluoropolymer coating over the base material.

2. The apparatus of claim 1 wherein the fluoropolymer coating is approximately 0.5-10  $\mu\text{m}$  thick.

3. A backing plate adapted to distribute gas as the gas flows into a processing chamber, the backing plate comprising:

interior surfaces that are exposed to gas entering the chamber; and

a fluoropolymer coating over a portion of the interior surfaces.

4. The apparatus of claim 3 wherein the fluoropolymer coating is approximately 0.5-10  $\mu\text{m}$  thick.

5. A system for processing a substrate within a chamber and for cleaning accumulated material layers from components of the chamber, comprising:

a reactive species generator adapted to generate a reactive species for chemically etching accumulated material; and

a processing chamber coupled to the reactive species generator and having at least one component having a continuously formed fluoropolymer coating thereon which is exposed to reactive species generated by the reactive species generator during cleaning.

6. The system of claim 5 wherein the processing chamber has a plurality of components which are exposed to the reactive species, wherein a percentage of the components exposed to the reactive species have a continuously formed fluoropolymer coating, and wherein the percentage is sufficient to increase the cleaning rate of the chamber.

7. The system of claim 6 wherein the percentage of coated components is sufficient to increase the cleaning rate of the chamber by at least 20%.

8. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a gas distribution plate having a plurality of apertures through which gas enters the deposition chamber.

9. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a backing plate.

10. The system of claim 8 wherein the at least one fluoropolymer coated component further comprises a backing plate.

11. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a shadow frame.

12. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a chamber wall liner.

13. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a susceptor.

14. The system of claim 5 wherein the at least one fluoropolymer coated component comprises a gas conductance line adapted to conduct a reactive species from the reactive species generator to the processing chamber.

15. A method for cleaning a processing chamber via a reactive species which chemically etches accumulated materials from chamber components, the method comprising:

providing a processing chamber adapted to perform a process by which material accumulates on chamber components;

supplying the processing chamber with at least one fluoropolymer coated component; and

cleaning the processing chamber with a reactive species which chemically etches accumulated material from chamber components;

wherein the fluoropolymer coated component is exposed to the reactive species.

16. A method of cleaning a processing chamber using a reactive species, the method comprising:

flowing an amount of fluoropolymer precursor gas into the processing chamber;

generating a plasma within the processing chamber so as to form fluoropolymer on chamber components;

heating the processing chamber so as to melt the fluoropolymer and form a fluoropolymer coating on the chamber components, wherein the amount of fluoropolymer precursor gas is controlled so as to form a uniform fluoropolymer coating of approximately 0.5-10  $\mu\text{m}$  on the chamber components;

thereafter processing one or more substrates within the processing chamber; and

thereafter flowing into the processing chamber reactive species and thereby cleaning accumulated material from the chamber components.

17. The method of claim 16 wherein the fluoropolymer coating is continuously formed.

18. The method of claim 1 wherein the fluoropolymer precursor gas is  $\text{CHF}_3$ .

19. The apparatus of claim 6 wherein the fluoropolymer is PTFE.

20. The apparatus of claim 6 wherein the fluoropolymer is FEP.

21. The apparatus of claim 6 wherein the fluoropolymer is PFA.

\* \* \* \* \*





INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C23C 16/44	A1	(11) International Publication Number: WO 99/20812 (43) International Publication Date: 29 April 1999 (29.04.99)
---	----	---

(21) International Application Number: PCT/US98/21806

(22) International Filing Date: 14 October 1998 (14.10.98)

(30) Priority Data:  
08/955,181 21 October 1997 (21.10.97) US

(71) Applicant: APPLIED MATERIALS, INC. [US/US]; 3050 Bowers Avenue, Santa Clara, CA 95054 (US).

(72) Inventors: YIN, Gerald, Zheyao; 10132 Bilich Place, Cupertino, CA 95014 (US). QIAN, Xue-Yu; 230 Rose Drive, Milpitas, CA 95035 (US). LEAHEY, Patrick, L.; 1715 Parkside Avenue, San Jose, CA 95125 (US). MOHN, Jonathan, D.; 13179 Paseo Presada, Saratoga, CA 95070 (US). CHOW, Waiching; 35875 Vivian Place, Fremont, CA 94536 (US). CHEN, Arthur, Y.; 744 Bodega Court, Fremont, CA 94539 (US). SUN, Zhi-Wen; 126 Destry Court, San Jose, CA 95136 (US). HATCHER, Brian, K.; 361 Springpark Circle, San Jose, CA 95136 (US).

(74) Agents: BERNADICOU, Michael, A. et al.; Blakely, Sokoloff, Taylor & Zafman LLP, 7th floor, 12400 Wilshire Boulevard, Los Angeles, CA 90025 (US).

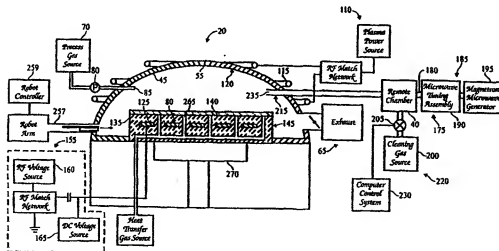
(81) Designated State: JP.

**Published**

*With international search report.*

*Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: METHOD FOR CLEANING AN ETCHING CHAMBER



**(57) Abstract**

An apparatus (20) and process for treating and conditioning an etching chamber (30), and cleaning a thin, non-homogeneous, etch residue on the walls (45) and components of the etching chamber (30). In the etching step, a substrate (25) is etched in the etching chamber (30) to deposit a thin etch residue layer on the surfaces of the walls and components in the chamber. In the cleaning step, cleaning gas is introduced into a remote chamber (40) adjacent to the etching chamber (30), and microwave or RF energy is applied inside the remote chamber to form an activated cleaning gas. A short burst of activated cleaning gas at a high flow rate is introduced into the etching chamber (30) to clean the etch residue on the walls (45) and components of the etching chamber. The method is particularly useful for cleaning etch residue that is chemically adhered to ceramic surfaces in the chamber, for example surfaces comprising aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, zirconium oxide, or mixtures thereof.

**APPENDIX B**

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## METHOD FOR CLEANING AN ETCHING CHAMBER

BACKGROUND

The present invention relates to an etching chamber and a method for etching substrates and for cleaning and conditioning the surfaces of the chamber.

In the manufacture of integrated circuits, silicon dioxide, polysilicon, tungsten silicide, and metal layers on a substrate, are etched in predefined patterns to form gates, vias, contact holes, or interconnect lines. In the etching process, a patterned mask layer, such as an oxide hard mask or a photoresist layer, is formed on the substrate using conventional photolithographic methods, and the exposed portions of the substrate are etched by capacitive or inductively coupled plasmas. Commonly used etchant halogen gases include fluorinated gases such as  $\text{CF}_4$ ,  $\text{SF}_6$ , and  $\text{NF}_3$ ; chlorinated gases such as  $\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{BCl}_3$ ; and brominated gases such as  $\text{HBr}$ ,  $\text{Br}$ , and  $\text{CH}_3\text{Br}$ .

In the etching process, the etching chamber is contaminated by a thin etch residue layer that deposits on the walls and other components in the chamber. The composition of the etch residue layer depends upon the etchant gases, the material being etched, and the composition of the mask layer applied to the substrate. When silicon is etched, silicon-containing gaseous species vaporized or sputtered from the substrate are present in the chamber environment; and when metal species are etched, metal ions are present in the chamber environment. The resist or mask layer on the substrate is also partially etched away by the etchant gas to form gaseous hydrocarbon or oxygen species in the chamber. These different species combine within the chamber

environment to form polymeric byproducts containing hydrocarbons, elemental silicon or metal species, and often also contain oxygen, nitrogen or boron. The polymeric byproducts deposit as thin etch residue layers on the walls and components in the chamber. The composition of the etch residue layer can vary

5 widely across the chamber depending upon the composition of the localized gaseous environment.

The non-homogeneous, etch residue layer formed in the etching process has to be periodically cleaned to prevent contamination of the

10 substrate, and to provide internal chamber surfaces that have consistent and homogeneous chemical compositions and surface functionality, otherwise the etching processes performed in the chamber can vary widely in etching properties. In a traditional wet cleaning process, an operator periodically shuts down the etching machine, and uses an acid or solvent to scrub down the

15 chamber walls. In the competitive semiconductor industry, the increased per substrate cost arising from downtime of the etching chamber, is undesirable. Also, because the wet cleaning process is manually performed by an operator, it often varies from one session to another, and limits the reproducibility of the etching process conducted in the chamber.

20

Another commonly used etch chamber cleaning method uses an in-situ ionized plasma which is generated inside the etch chamber, to clean the chamber walls. However, the in-situ ionized plasma species are highly energetic and can rapidly erode the chamber walls and chamber components. It is

25 expensive to periodically replace the eroded parts and components in the chamber. Also, surface erosion of the chamber surfaces and components by the energetic plasma species, can often result in the instability and lack of reproducibility of subsequent plasma etching process steps performed in the chamber. For example, variations in the concentration, type, or surface

30 functional bonds or chemical groups on the exposed surfaces of the walls and

components in the chamber, affect the sticking coefficient of gases and vapors on these surfaces, and consequently, the gaseous plasma etching chemistry in the chamber. Chamber surfaces having excessively active surface functional groups can deplete the concentration of gaseous chemical species needed to etch the substrate. Furthermore, the relatively high plasma power levels required to achieve acceptable cleaning rates tend to generate residue byproducts that damage system components and which cannot be removed except by physically wiping the internal surfaces of the chamber. For example,  $\text{NF}_3$  plasma used to clean aluminum chamber surfaces results in formation of  $\text{Al}_x\text{F}_y$  compounds that cannot be etched away by nonchemical processes. As another example,  $\text{NF}_3$  gas that is used to clean  $\text{Si}_3\text{N}_4$  CVD deposition systems result in formation of  $\text{N}_x\text{H}_y\text{F}_z$  compounds that are deposited on the exhaust or vacuum pump and affect the reliability of the exhaust pump.

In chemical vapor deposition (CVD) processes, cleaning gases that are activated by microwaves in a remote chamber and further energized by capacitive coupled plasmas in-situ in the CVD chamber, have been used to clean the relatively thick and homogeneous CVD deposit layers formed in these chambers. In a typical CVD process, reactive gases are used to deposit a layer of material, such as aluminum or silicon dioxide, on the substrate. During the deposition process, the CVD deposits that are formed on the chamber walls and surfaces are often as thick as the CVD layers deposited on the substrate. The CVD deposits also have a relatively uniform and homogeneous chemical composition that corresponds to the material deposited on the substrate. The thick and chemically homogeneous CVD deposits can be cleaned by a high power microwave and capacitive coupled plasma, as for example, described in U.S. Patent No. 5,449,411, which is incorporated herein by reference. In another example, commonly assigned European Patent No. 555 546 A1 discloses a process for CVD of silicon and removal of silicon deposits from the walls of the CVD chamber using a microwave plasma of  $\text{NF}_3$  or  $\text{CF}_4/\text{O}_2$ .

Similarly, German Patent No. 4,132,559 A1 also describes a method of cleaning a CVD deposition chamber using a remotely generated microwave plasma of  $\text{NF}_3$ .

5                   However, the CVD chamber cleaning processes for cleaning thick and stoichiometrically homogeneous CVD deposits in deposition chambers are not suitable for cleaning the thin, variable composition, etch residue layers formed on the inner surfaces of etching chambers. The thin etch residue layers make it difficult to stop the cleaning process, after removal of the residue layer, 10 resulting in extensive erosion of the underlying chamber surfaces. Also, the variable chemical stoichiometry and composition of the etch residue layers at different portions of the chamber make it difficult to clean all of the residue. For example, the etch residue formed near the chamber inlet or exhaust is often thinner and has a higher concentration of etchant gas species (or of material 15 being etched) than etch residue formed near the substrate which typically contains a higher concentration of polymeric or oxide mask species. It is extremely difficult to generate a plasma or gas that uniformly etches away the variable stoichiometric composition etch residue without either eroding the chamber walls below the thin soft residue layers, or conversely, failing to clean- 20 off thick and chemically hard residue layers. For these reasons, known methods of cleaning CVD deposits in deposition chambers are ineffective at cleaning the ultra thin and compositional variant etch residue layers formed on the walls and components of etching chamber without damaging or eroding the underlying walls and component surfaces.

25                   Thus, it is desirable to have a treatment process that maximizes the chemical reactivity of the cleaning gas to etchant deposits in an etching chamber and that minimizes the chemical reactivity of the cleaning gas to the exposed surfaces in the chamber. It is further desirable to have a method for 30 treating the etching chamber that removes chemically adhered etchant deposits

from chemically active surfaces in the chamber and restores the original chemical reactivity and surface functional groups of these surfaces. It is further desirable for the chamber cleaning process to remove etch residues having variable thickness and non-uniform chemical stoichiometry, without excessive erosion of the chamber walls and components.

### SUMMARY

The present invention provides an apparatus and method of etching a substrate in an etching chamber, cleaning a non-homogeneous, variable composition, etch residue layer from the walls and components of an etching chamber, and treating and conditioning ceramic surfaces in the chamber to provide highly consistent and reproducible etching performance. In the etching step, a substrate is etched in the etching chamber thereby depositing a thin etch residue layer on the surfaces of the walls and components in the etching chamber. In the cleaning step, cleaning gas is activated in a remote chamber adjacent to the etching chamber, for example, by applying microwave or RF energy in the remote chamber. The activated cleaning gas is introduced into the etching chamber to clean the etch residue on the walls and components of the etching chamber. It has been discovered that this method is particularly useful for cleaning etch residue strongly adhered to, or chemically reacted with, ceramic surfaces comprising aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, zirconium oxide, or mixtures thereof.

When etching certain materials, for example, silicon-containing layers, a relatively thin etch residue layer containing primarily polymeric, oxygen, and silicon-containing species, and having a thickness of about 0.01 to about 1 micron is formed on the chamber walls and surfaces. It has been discovered that such an etchant layer can be efficiently removed by a high flow rate, short

burst of activated cleaning gas introduced into the etching chamber at a flow rate  $F_R$  equivalent to a rate of about 200 to about 2000 sccm for a chamber having a volume of about 40,000 cm<sup>3</sup> for a time period of about 0.5 to about 100 seconds to clean the etch residue, substantially without eroding the walls and components in the chamber.

Preferably, the cleaning process is performed while or immediately after, the substrate is being transported out of the etching chamber, to increase throughput from the etching chamber. Preferably, a short burst of a high flow rate of activated cleaning gas is introduced into the etching chamber for a short time period, while substrate is being transported in or out of the chamber, to clean and condition the surfaces in the chamber without eroding chamber surfaces or substrate surfaces. Another substrate is then transported into the chamber and the etching, transportation, and cleaning and conditioning steps are repeated, until the substrate supply is exhausted. In a preferred version, the remote chamber is maintained at a higher pressure than the etch chamber, to provide a more laminar flow of cleaning gas along the sidewalls and surfaces of the chamber.

It has further been discovered, in accordance with another aspect of the present invention, that superior cleaning and conditioning of etching chamber surfaces that are highly reactive to etch residue is achieved by introducing the activated gas into the chamber in multiple and discrete stages. The multicycle conditioning process comprises (i) a first stage, in which a first activated cleaning gas formed by maintaining the gas activator in the remote chamber at a first power level, is introduced into the etching chamber; and (ii) at least one second stage, in which a second activated cleaning gas formed by maintaining the gas activator in the remote chamber at a second power level different from the first power level, is introduced into the etching chamber. The cleaning gas in the first stage contains a more dissociated and chemically



reactive species that removes the hard and thick etch residues at the chamber walls and components near the substrate. The cleaning gas in the second cleaning stage is activated at a lower power level to more gently treat and condition surfaces such as ceramic surfaces. The duration of each cleaning stage is from about 0.5 to about 100 seconds, and more preferably, from about 0.5 to about 24 seconds. The multicycle process can be repeated a sufficient number of times to treat the chamber walls and reduce the concentration of etch residue to the desirable level.

10 In yet another aspect, the present invention is to an etching apparatus comprises an etching chamber having a process gas inlet for introducing process gas into the chamber, a plasma generator for forming a plasma from the process gas for etching a substrate, and an exhaust system for exhausting the spent process gas from the etching chamber. A remote chamber  
15 adjacent to the etching chamber is used to generate an activated cleaning gas. A gas distribution system comprises (i) a gas conduit for transporting the activated cleaning gas from the remote chamber to the etching chamber, (ii) a gas flow distributor for directing the flow of activated cleaning gas substantially parallel, and adjacent to, one or more internal surfaces of the chamber, and  
20 (iii) a gas flow regulator for regulating the flow of activated cleaning gas into the gas flow distributor. Preferably, the gas flow distributor has nozzles positioned adjacent to surfaces in the chamber that have thicker etch residue layers, for directing the flow of activated cleaning gas to these regions to preferentially remove the thicker etch residue layers without eroding portions of the chamber  
25 having thinner etch residue layers.

DRAWINGS

These and other features, aspects, and advantages of the present invention will be better understood from the following drawings, description and appended claims, which illustrate examples of the invention. While the description and drawings below illustrate exemplary features of the invention, it is to be understood that each of the features can be used in the invention in general, not merely in the context of the particular drawings, and the invention includes any combination of these features.

Figure 1 is a sectional schematic side view of an etching apparatus of the present invention;

Figure 2 is a flowchart of the process steps used to etch substrates and clean and condition the surface walls of the etching apparatus;

Figure 3 is a sectional schematic side view of another version of an etching apparatus of the present invention;

Figure 4 is a sectional schematic side view of another version of an etching apparatus of the present invention;

Figure 5 is a sectional schematic view of another version of an etching apparatus of the present invention; and

Figure 6 is a sectional schematic view of another version of an etching apparatus of the present invention.

DESCRIPTION

An apparatus 20 suitable for etching a substrate 25 according to the present invention, as schematically illustrated in Figure 1, comprises an enclosed process chamber 30 defining a process zone for processing the substrate, a remote chamber 40 for forming an activated cleaning gas, and a load-lock transfer area (not shown) maintained at low pressure for holding a cassette of substrates. The particular embodiment of the apparatus 20 shown herein is suitable for processing of semiconductor substrates 25 is provided only to illustrate the invention and should not be used to limit the scope of the invention. Particular features of the apparatus 20 are described in U.S. patent application serial no. 08/597,445, entitled "RF Plasma Reactor with Hybrid Conductor and Multi-Radius Dome Ceiling," filed on February 2, 1996; and in U.S. patent application serial no. 08/389,889, filed on February 15, 1993 -- both of which are incorporated herein by reference. The enclosed chamber 30 has sidewalls 45 and a bottom wall 50 fabricated from any one of a variety of materials including metals, ceramics, glasses, polymers, and composite materials. The process zone defined in the etching chamber 30 is directly above and surrounds the substrate 25 and comprises a volume of at least about 10,000 cm<sup>3</sup>, and more preferably about 10,000 to about 50,000 cm<sup>3</sup>. Metals commonly used to fabricate the enclosed chamber 30 include aluminum, anodized aluminum, "HAYNES 242," "Al-6061," "SS 304," "SS 316," and INCONEL, of which anodized aluminum is preferred.

The process zone comprises a ceiling 55 that is flat or rectangular shaped, arcuate, conical, dome-shaped, or multiradius dome shaped. Preferably, the ceiling 55 is dome-shaped to provide a uniform distribution of plasma source power across the entire volume of the plasma process zone to increase dissociation of the etchant gas within the plasma zone, as for example described in U.S. patent application Serial No. 08/596,960, entitled "Plasma

Process for Etching Multicomponent Alloys," filed on February 5, 1996, to Ma et al., which is incorporated herein by reference. The dome-shaped ceiling 55 reduces dissociated ion recombination losses near the substrate 25 so that plasma ion density is more uniform across the substrate than with a flat ceiling.

5 This is because ion recombination losses are affected by the proximity of the ceiling 55, and the dome-shaped ceiling is further from the substrate center 60 than a flat ceiling. The dome ceiling 55 can be planar (i.e., flattened dome), conical, truncated conical, cylindrical, or other combination of such shapes, that provides a dome shaped surface above the substrate 25.

10

Process gas is introduced into the chamber 30 through a gas distribution system 65 that includes a process gas supply 70 and a gas flow control system 75 that operates gas flow meters 80. The gas distribution system 65 can comprise gas outlets 85 located peripherally around the

15 substrate 25 (as shown), or a showerhead mounted on the ceiling of the chamber 30 with outlets therein (not shown). Spent process gas and etchant byproducts are exhausted from the process chamber 30 through an exhaust system 90 (typically including a 1000 liter/sec roughing pump) capable of achieving a minimum pressure of about  $10^{-3}$  mTorr in the chamber 30. A

20 throttle valve 95 is provided in the exhaust 90 to control the flow of spent process gas and the pressure of process gas in the chamber 30. Preferably, an asymmetric pumping channel 100 is used to pump gases out of the chamber 30 to provide a more symmetrical and uniform distribution of gaseous species around the surface 105 of the substrate.

25

A plasma is formed from the process gas introduced into the chamber 30, using a plasma generator 110 that couples an electric field into the process zone of the chamber. A suitable plasma generator 110 comprises an inductor antenna 115 consisting of one or more inductor coils having a circular

30 symmetry with a central axis coincident with the longitudinal vertical axis that

extends through the center of the process chamber 30 and perpendicular to the plane of the substrate 25. Preferably, the inductor antenna 115 comprises solenoid coils having from 1 to 10 turns, and more typically from 2 to 6 turns. The arrangement and number of solenoid coils are selected to provide the  
5 desired product of current and antenna turns  $(d/dt)(N \cdot I)$  near the ceiling 55 to provide a strong inductive flux linkage with close coupling to the plasma and therefore greater plasma ion density in the plasma zone adjacent to the substrate 25, as described in U.S. patent application no.08/648,254. When the inductor antenna 115 is positioned near the dome ceiling 55, the ceiling of the  
10 chamber 30 comprises dielectric material which is transparent to RF fields, such as a slab of machined silicon dioxide or tiles of silicon or silicon dioxide bonded to one another to provide a curved shape. Preferably, the inductor coil 115 wrapped around the sidewall 45 of the process chamber 30 is a multiradius dome-shaped inductor coil having a "flattened" dome shape that provides  
15 increased plasma ion density directly over the substrate center 60 because ion density is affected by local ionization near the inductor coil 115, and a multiradius inductor coil is closer to the substrate center 60 than a hemispherical coil. In another preferred embodiment, the ceiling 55 comprises a multiradius dome having at least a center radius  $R$  and a corner radius  $r$ , wherein  
20  $r$  is less than the center radius  $R$  and  $R/r$  is from about 2 to about 10.

The plasma formed in the plasma zone can also be enhanced using magnetically enhanced reactors, in which a magnetic field generator (not shown), such as a permanent magnet or electromagnetic coils, are used to apply  
25 a magnetic field in the plasma zone to increase the density and uniformity of the plasma. Preferably, the magnetic field comprises a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate 25, as described in U.S. Patent No. 4,842,683, issued June 27, 1989, which is incorporated herein by reference. The magnetic field in the chamber 30 should  
30 be sufficiently strong to increase the density of the ions formed in the plasma,

and sufficiently uniform to reduce charge-up damage to features such as CMOS gates. Generally, the magnetic field as measured on the surface 105 of the substrate is less than about 500 Gauss, more typically from about 10 to about 100 Gauss, and most typically from about 10 Gauss to about 30 Gauss.

5

In addition to the inductor antenna 115, one or more process electrodes can be used to accelerate or energize the plasma ions in the chamber 30. The process electrodes include a first electrode 120 forming a wall of the process chamber 30, such as the ceiling 55 and/or sidewalls 45 of the chamber. 10 The first electrode 120 is capacitively coupled to a second electrode 125 below the substrate 25. An electrode voltage supply 155 supplies an RF potential that maintains the first and second electrodes 120, 125 at different electrical potentials relative to one another. The frequency of the RF voltage applied to the inductor antenna 115 is typically about 50 KHz to about 60 MHz, and more 15 typically about 13.56 MHz; and the power level of RF voltage applied to the antenna is about 100 to about 5000 Watts.

The enclosed chamber 30 comprises one or more ceramic surfaces that serve different functions. For example, in one preferred embodiment, the 20 walls 45, 50, 55 of the process chamber are coated with a ceramic material, such as boron carbide, boron nitride, silicon, silicon oxide, silicon carbide, or silicon nitride, to protect the walls from chemically erosion in particular etchant gas compositions. For example, boron carbide is useful for protecting sidewalls 45 of chambers from erosion in fluorinated gaseous environments. As another 25 example, sapphire (aluminum oxide) gas distribution plates can be used to release process gas into the chamber 30.

Another ceramic surface useful in the process chamber 30 is that of a monolithic ceramic member 135 having a ceramic receiving surface 140 for 30 receiving a substrate 25 thereon. Suitable ceramic materials include one or

more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide. The ceramic member 135 is fabricated from a low porosity ceramic having a porosity of less than about 10%. The thermal conductivity of the dielectric material preferably comprises a high conductivity of about 80 to about 240 Watts/m K, for example, diamond or aluminum nitride. The second electrode 125 is embedded in the ceramic member 135 so that ceramic material completely surrounds the second electrode to form a unitary monolithic ceramic member. The second electrode 125 is fabricated from a conductive metal such as aluminum, copper, gold, molybdenum, tantalum, titanium, tungsten, and alloys thereof, and more preferably from a high melting point refractory metal, such as tungsten, tantalum or molybdenum, which allows thermal sintering of the ceramic member 135 with the embedded electrode 125 therein. The ceramic member 135 with the embedded electrode 125 can be fabricated by isostatic pressing, hot pressing, mold casting, or tape casting, from a mixture of ceramic powders and a low concentration of organic binder material.

The embedded second electrode 125 in the unitary monolithic ceramic member 135, is the sole conductor to which a "hot" RF potential is applied, with the other electrodes in the chamber 30 maintained at different potentials, including electrical ground or floating potentials, relative to the second electrode 125. Because it is embedded in the unitary ceramic member 135, the second electrode 125 does not have to be electrically isolated from the chamber 30 by additional insulator shields, thereby reducing the parasitic capacitance impedance loads in the chamber 30 that would otherwise result between the second electrode 125 and the grounded chamber walls 45, 50. Also, because there is no insulator shield in the chamber 30, the active area of the second electrode 125 can be increased to cover an area having a diameter that extends across the entire chamber bottom 50, providing a larger active

electrode area than conventional cathodes. The second electrode 125 also serves as an electrostatic chuck 145 that generates an electrostatic charge for electrostatically holding the substrate 25 to the receiving surface 140 of the ceramic member 135 using a DC chucking voltage applied through an electrical conductor 150 inserted through the ceramic member 135 to connect to the second electrode 125.

The first and second electrodes 120, 125 are electrically biased relative to one another by the electrode voltage supply 155 that includes an AC voltage 160 supply for providing a plasma generating RF voltage to the second electrode 125, and a DC voltage supply 165 for providing a chucking voltage to the electrode 125. The AC voltage supply 160 provides an RF generating voltage having one or more frequencies from 13.56 MHZ to 400 KHz to form a capacitively coupled plasma in the chamber 30. The power level of the RF bias current applied to the electrode 125 is typically from about 50 to about 3000 Watts. A separate DC voltage is applied to the electrode 125 to form an electrostatic charge that holds the substrate 25 to the chuck 145. The RF power is coupled to a bridge circuit and an electrical filter to provide DC chucking power to the electrode 125.

The etching apparatus 20 further comprises a remote chamber 40, such as a quartz tube, adjacent and connected to the process zone of the etching chamber 30 via a gas conduit 170. The remote chamber 40 comprises a gas activator 175 that is used to provide a microwave or RF energy in the chamber 30, to activate the cleaning gas by ionization or dissociation. When microwave energy is supplied, the cleaning gas dissociates to form uncharged atomic species, for example,  $\text{Cl}_2$  dissociates to form atomic chlorine. When an RF energy is applied to the remote chamber 40, for example, by induction or capacitive coupling, the cleaning gas forms charged ionized species in the remote chamber.



Preferably, the gas activator 175 provides microwaves that chemically activate the cleaning and conditioning gas in the remote chamber by formation of a highly dissociated gas. In this version, as schematically illustrated in Figure 1, the gas activator 175 comprises a microwave waveguide 5 180 powered by a microwave generator 185, such as the "ASTEX" Microwave Plasma Generator commercially available from the Applied Science & Technology, Inc., Woburn, Massachusetts. Typically, the microwave generator 185 comprises a microwave tuning assembly 190 and a magnetron microwave generator 195 capable of generating microwaves at a frequency of 2.54 Ghz. 10 Typically, the magnetron 195 comprises a high power microwave oscillator in which the potential energy of an electron cloud near a central cathode is converted into microwave energy in a series of cavity resonators spaced radially around the cathode. The resonant frequency of the magnetron 195 is determined by the physical dimensions of the resonator cavities.

15

A second gas supply system 200 provides a cleaning gas to the remote chamber 40 via an electronically operated valve 205 and flow control mechanism at a user-selected flow rate. The microwave generator control system then applies power to the microwave generator 185 to generate 20 microwaves which are transported by the waveguide 180 to the remote chamber 40. The activated cleaning gas is transported from the remote chamber 40 to the etching chamber 30 via a gas distribution system comprising the gas conduit 170. Optionally, a filter is positioned in the conduit 170 through which the activated gas species passes before entering the etching 25 chamber 30 to remove particulate matter that is formed during the activation of the reactive species. In the described embodiment, the filter is made of ceramic material having a pore size of about 0.01 to 0.03 microns. Other materials can also be used, such as Teflon (TM DuPont de Nemours, Inc.), polyimide, inactivated carbon, or sulphur. For example, when the cleaning gas comprises 30  $\text{CF}_4$  or  $\text{SF}_6$ , or other halogen compounds containing carbon or sulphur, an

activated carbon of sulphur species is often present as a byproduct of the activation process. It is generally desirable to remove such carbon or sulphur products to prevent contamination of the etching chamber environment.

5                   Instead of using microwaves, the cleaning gas can also be activated by an RF energy provided by a capacitively or inductively coupled source in or adjacent to the remote chamber 40. A suitable RF energy type gas activator comprises an inductor antenna consisting of one or more inductor coils having a circular symmetry with a central axis coincident with the longitudinal  
10                  vertical axis that extends through the center of the remote chamber 40, as shown in Figure 4. Alternatively, the gas activator can also comprise a pair of electrodes positioned within the remote chamber 40 to form a capacitively coupled field in the chamber 40, as shown in Figure 3.

15                   The gas distribution system further comprises a gas flow distributor 215 for directing the flow of activated cleaning gas substantially parallel, and adjacent to, one or more internal surfaces of the chamber 30 and a gas flow regulator 220 for regulating the flow of activated cleaning gas into the gas flow distributor 215. The gas flow regulator comprises a flow control valve  
20                  205 or 225 operated by a conventional computer control system 230 to control the flow of the cleaning gas into the remote chamber 40 at a predefined or user-selected gas flow rate. Optionally, a carrier gas source can also be connected to the remote activation chamber 40 through another valve and flow control mechanism (not shown). The carrier gas assists in transporting the activated  
25                  cleaning gas to the etching chamber 30, and can be any known gas that is non-reactive or compatible with a particular cleaning process. For example, a suitable carrier gas can be argon, nitrogen, helium, halogen, or oxygen. The carrier gas can also assist in the cleaning process by initiating and/or stabilizing the activated gaseous species in the etching chamber 30.

Preferably, the gas flow distributor 215 directs the flow of the activated cleaning gas generally parallel, or adjacent to, one or more of the surfaces inside the chamber 30, such as the surfaces of the sidewall 45, the bottom surface 50, or the surfaces of components in the chamber. Directing the flow of cleaning gas substantially parallel to certain chamber surfaces provides a more concentrated and laminar flow of cleaning gas adjacent to these surfaces that removes the etch residue and treats and conditions the chamber surfaces more effectively. In the version shown in Figure 3, the gas distributor comprises a plurality of gas injection nozzles 235a, b, c, arranged symmetrically about a central axis of the chamber 30, to provide a laminar curtain of gas flowing immediately past, adjacent, and substantially parallel to the surfaces of the etching chamber 30 to enhance cleaning of the etch residue on the chamber walls. The gas injection nozzles 235a, b, c provide a cleaning gas flow pattern or flow pathway that is directed along the walls and surfaces of the chamber that have a high concentration, thickness, or more chemically hard composition of etch residue, to preferentially clean and condition these surfaces, with excessive erosion of other portions of the chamber that have less etch residue.

In another version, shown in Figure 4, the gas distributor 215 comprises one or more gas injection nozzle 235 that is positioned behind a gas spreading or flow redirecting plate 240 in the chamber 30. The gas spreading plate 240 is symmetrically positioned in the chamber with preferably a perpendicular central axis that is substantially aligned to the central axis of the chamber 30. The plate 240 covers the gas injection nozzle 235 and deflects and redirects the flow of cleaning gas emitted from the injection nozzles 235, between the gap defined by the plate and a parallel portion of the chamber surface adjacent to the plate 240. The gas spreader plate 240 is spaced apart and at a predefined distance from the chamber surface to define a gap having a predefined height. The cleaning gas exits the annular ring-shaped outlet defined by the plate 240 and the chamber surface substantially parallel to the chamber

surface, and flows in a laminar flow path along the surface of the etching chamber walls.

In yet another configuration, illustrated in Figure 5, the gas distributor 215 comprises injection nozzles 235a, b at the terminus of a channel 250 that is symmetrically positioned about a central axis of the chamber 30. An annular ledge 255 is spaced apart from, and preferably covers, at least a portion of the channel 250 to form a circumferential collar that directs the flow of cleaning gas along and past particular surfaces of the chamber 30 to recondition and treat these surfaces. As with the gas plate version illustrated in Figure 4, the annular opening of the channel 250 adjacent to the chamber surfaces, provides a forced flow of cleaning gas past the chamber surfaces.

Preferably, the gas flow distributor 215 comprises gas injection nozzles 235 that are positioned adjacent to surfaces in the chamber 30 that have thicker etch deposit layers, for directing the flow of activated cleaning gas to these regions to preferentially remove the thicker etch residue layers without eroding portions of the chamber 30 having thinner deposit layers. This is particularly useful for etching chambers and processes that produce widely varying composition or thickness of etch residue deposit layers across the surfaces of the chamber 30. Typically, the thicker etch residue regions are adjacent to the substrate, where a larger quantity of resist or mask vaporizes from the substrate, and condenses onto the chamber surfaces. For example, in a preferred configuration, as shown in Figure 6, the gas injection nozzles 235a, b are positioned in a circle that surrounds the substrate 25 and extend from the bottom wall 50 of the chamber 30. This configuration is preferred for etching processes in which a large amount of etch residue is formed near the chamber surfaces that are next to the substrate, because the etch residue is a condensation byproduct of the resist or oxide mask on the substrate. Similarly, the gas injection nozzles 235a, b can be positioned in the other regions of the

chamber 30 as determined from the distribution and etch residue across the chamber surfaces for each type of etch process.

### Etching Process

5

Operation of the etching chamber 30 to etch one or more of the silicon-containing layers on the substrate 25 will now be described with reference to the flow chart of Figure 2. The substrate 25 typically comprises a semiconductor material, such as a silicon or gallium arsenide wafer, with a plurality of layers formed thereon. The layers on the substrate 25 comprise, for example, an underlayer of silicon dioxide that functions as a gate oxide layer for MOS transistors, and an overlayer of polysilicon or patterned polycide (which is a combination of tungsten silicide and underlying polysilicon layers). Each of the layers typically have a thickness of about 100 nm to about 350 nm. A mask layer, such as "RISTON" photoresist manufactured by DuPont de Nemours Chemical Company, or an oxide hard mask is applied over the substrate 25 to a thickness of about 0.4 to about 1.3 micron; and the features to be etched in the layers are defined using conventional photolithographic processes. The exposed portions between the mask layer are etched to form features, such as for example, contact holes for fabricating gate electrodes for MOS transistors; polycide interconnecting features that are typically used as gate electrodes; and vias which are multilayer metal structures used to electrically connect two or more electrically conductive layers separated by insulating silicon oxide/nitride layers.

25

To perform the process of the present invention, a substrate 25 is transferred using a robot arm 257 from a load-lock transfer chamber through a slit valve and into the chamber 30. A lift finger assembly (not shown) has lift fingers that extend through lift finger openings in the chuck 145 to receive or lift the substrate 25 off the chuck 145. The robot arm 257 places the substrate

30

25 on the tips of the lift fingers (not shown) that are elevated by the pneumatic lift mechanism to extend about 2 to 5 centimeters above the surface of the chuck 145. The pneumatic mechanism, under the control of a computer system, lowers the substrate 25 onto the electrostatic chuck 145, and helium is supplied through apertures 265 in the chuck to control the temperature of the substrate 25.

Etchant gas is introduced into the chamber 30 through the gas outlet 85, and the chamber is typically maintained at a pressure ranging from about 0.1 to about 400 mTorr, and more typically from about 0.1 to 80 mTorr. Suitable halogen-containing etchant gases for etching the substrate 25, include for example, HCl, BCl<sub>3</sub>, HBr, Br<sub>2</sub>, Cl<sub>2</sub>, CCl<sub>4</sub>, SiCl<sub>4</sub>, SF<sub>6</sub>, F, NF<sub>3</sub>, HF, CF<sub>3</sub>, CF<sub>4</sub>, CH<sub>3</sub>F, CHF<sub>3</sub>, C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>F<sub>6</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>8</sub>, C<sub>2</sub>HF<sub>5</sub>, C<sub>4</sub>F<sub>10</sub>, CF<sub>2</sub>Cl<sub>2</sub>, CFCI<sub>3</sub>, and mixtures thereof. The etching process of the present invention provides high etch rates, and highly selective etching of the silicon layers on the substrate 25. A preferred composition of process gas comprises (i) chlorine, (ii) hydrogen bromide, and optionally (iii) helium-oxygen gas. The chlorine gas is ionized to form atomic chlorine and chlorine-containing species that etch the metal silicide or polysilicon layers to form volatile SiCl<sub>x</sub> species that are exhausted from the chamber 30. The chlorine gas can comprise Cl<sub>2</sub> or other chlorine-containing gases equivalent to chlorine, for example, HCl, BCl<sub>3</sub>, and mixtures thereof. The hydrogen bromide gas enhances the rate of etching of the polysilicon layer while simultaneously reducing the rate of etching of the resist layer to enhance the etching selectivity ratio. The helium-oxygen gas forms excited species and ions that further aid etching rates and etching selectivity.

Referring to Figure 2, a plasma is energized from the etchant gas using the plasma generator 110 by forming an inductive electric field in the chamber 30 and biasing the first and second electrodes 120, 125 in the chamber. The plasma is formed by applying an RF source current to the

inductor antenna 115 encircling the chamber 30, and applying an RF bias voltage to the electrodes 120, 125. The etchant gas ionizes in the applied electric field to form halogen-containing ions and neutrals that react with the silicon-containing layers on the substrate 25 to etch the layers and form volatile gaseous species that are exhausted from the chamber 30. Preferably, the power ratio  $P_r$  of the source current power level (to inductor antenna 115) to the bias voltage power level (to the process electrodes 120, 125) is selected to enhance the ability of the etchant plasma to anisotropically etch the silicon-containing layers with high selectivity relative to the overlying mask layer.

Increasing the source power level of the current applied to the inductor antenna 115, increases the number of dissociated etchant species in the plasma providing more isotropic etching. In contrast, increasing the bias power level of the RF voltage applied to the process electrodes 120, 125 increases the degree of anisotropic etching by providing a higher bombardment energy component to the plasma ions. It has been discovered that an excessively high power ratio  $P_r$  can cause sputtering of the substrate 25 and result in non-uniform etching of the substrate; while an excessively low power ratio  $P_r$  can cause insufficient dissociation of the etchant gas into dissociated ions resulting in low etch rates and low etching selectivity. A preferred power ratio  $P_r$  is at least about 2:1, and more preferably about 2:1 to about 20:1. The plasma is formed by applying a current at a source power level of about 400 to about 3000 Watts to the inductor antenna 115 encircling the plasma zone 35; and the plasma ions are attracted toward the substrate 25 by applying a voltage at a power level of about 20 to about 1000 Watts to the process electrodes 120, 125 in the plasma zone.

The substrate 25 etching process is typically performed in a main etch stage and an "overetch" stage, in order to stop the etching process without etching through the underlayer on the substrate. The main etch stage is stopped immediately before the overlayer is completely etched through, and

the overetch stage is performed to etch through the residual portion of the overlayer. Typically, the halogen content of the etchant gas is reduced in the overetch stage to obtain slower and more controllable etch rates. For example, a suitable main etch process stage for etching a polysilicon layer an etchant gas comprising 68 sccm  $\text{Cl}_2$ , 112 sccm  $\text{HBr}$ , and 16 sccm  $\text{He-O}_2$  can be used. The power level of the source current applied to the inductor antenna 115 is 475 Watts, and the power level of the bias voltage applied to the process electrodes 120, 125 is 80 Watts to provide a power ratio  $P_r$  of about 6:1. The pressure in the chamber 30 is held at 4 mTorr. A suitable over-etch process stage for the polysilicon layer uses an etchant process gas comprising 158 sccm  $\text{HBr}$  and 10 sccm  $\text{He-O}_2$  at a chamber pressure of 50 mTorr. The power level of the source current applied to the inductor antenna 115 was 1000 Watts, and the power level of the bias voltage applied to the process electrodes 120, 125 was 100 Watts to provide a power ratio,  $P_r$  of about 10:1, in the overetch process stage.

15 An optical endpoint measurement technique is used to determine completion of the entire etching process, or completion of etching of a specific layer by measuring the change in light emission of a particular wavelength corresponding to a detectable gaseous species. A sudden decrease or increase in concentration of a selected detectable species, indicates completion of etching of one or more of the layers. For example, a sudden increase in the concentration of silicon species (that results from chemical reaction of the process gas with the underlying polysilicon) indicates completion of the etching process; and an increase in chlorine ion concentration (resulting from reduced erosion of the underlayer) indicates completion of etching of the metal silicide layer and start of etching of the underlayer.

25 After completion of processing, the pneumatic lifting apparatus 270 raises the lift pins through the electrostatic chuck 145 to raise the substrate 25 and a robotic transport arm is inserted between the substrate 25



and the chuck to lift the substrate off the lift pins. Thereafter, the lift pins are retracted into the chuck 145, and the robotic arm transports the substrate 25 out of the etching chamber 30 and into a transfer chamber maintained in a vacuum environment.

5

#### Cleaning & Conditioning Process

Thereafter, a treatment process is used to treat and recondition the surfaces inside the etching chamber 30, particularly the ceramic surfaces; and to clean the etch residue formed on the chamber walls 45, 50, 55 and components. The etch residue adheres and reacts with the surfaces inside the etching chamber 30, for example, the sidewalls 45, receiving surface 140 of the monolithic ceramic member 135, and the ceiling 55 of the chamber, to form a hard and chemically resistant layer that is difficult to remove. The etch residue typically comprise polymeric organic compounds containing halogen, carbon, hydrogen, oxygen, and/or silicon compounds that are formed during etching of the substrate 25. In particular, the etch residues react with the ceramic surfaces in the chamber 30 such as the surfaces of the monolithic ceramic member 135, which have highly reactive surface functional groups. For example, ceramic surfaces comprising silicon or silicon oxide comprise Si-OH<sup>+</sup> surface groups which are formed when the ceramic surface is exposed to air, oxygen, or ambient moisture; and aluminum oxide or aluminum nitride surfaces have Al-OH<sup>+</sup> surface groups. These surface functional groups chemically react with the etch residue to form a hard adherent coating on the chamber surfaces or components.

25

The chamber treatment process treats the chamber 30 to remove and reduce the adverse effect of the reaction byproducts of the etch residues and the chamber surfaces will now be described. To perform the process, the process chamber 30 is exhausted of etchant gas by fully opening the throttle

30

valve 95 of the exhaust system 90. Cleaning gas, such as  $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$  or mixtures thereof, is introduced into the remote chamber 40 and activated therein, for example, by microwaves applied within the remote chamber by the microwave generator 185, or by RF energy applied via electrodes or an inductor coil. Thereafter, the activated cleaning gas is introduced into the etching chamber 30 to clean the etch residue in the chamber.

The power level  $P_L$  of the current used to operate the gas activator 175 is selected to achieve two functions. In a first function, the cleaning gas should chemically react with and vaporize the thin layer of etch residue comprising polymer containing carbon, trapped halogen species, silicon, and/or hydrogen species, formed on the chamber surfaces. The flow rate  $F_R$  of cleaning gas, and the power level  $P_L$  of the gas activator 175 control the ratio of dissociated to non-dissociated species in the activated cleaning gas. The more highly dissociated gaseous species preferentially react with the thin etchant layer relative to the underlying chamber surfaces. That is why the activated plasma can remove thin layers of etch residue on the chamber walls, while minimizing erosion of the underlying chamber surfaces. In a second function, the activated cleaning gas reconditions the surfaces in the chamber 30, particularly the ceramic surfaces, after removing the etch residue. It has been discovered that halogen containing etch residue is highly chemical reactivity to the chamber walls 45, 50, 55 and components, particularly when the etching chamber 30 contains ceramic surfaces that have highly reactive surface functional groups, such as the aforementioned  $\text{Si-OH}^+$ ,  $\text{Al-OH}^+$ , and other such species. For example, fluorine containing species in the etch residue rapidly erode ceramic aluminum oxide or nitride surfaces to form volatile  $\text{AlF}_3$  species. Similarly, bromine containing species hydrolyze in ambient moisture to form acidic hydrogen bromide which corrodes silicon-containing components. These types of etch residues need to be rapidly removed from the chamber 30 to

prevent excessive erosion of the chamber surfaces. A high flow rate  $F_R$  and low power level  $P_L$  activated gas species conditions the chamber surfaces, i.e., restores at least a portion of the surface functional groups, such as  $AlOH$  groups, on the ceramic surfaces in the chamber 30. This returns the chamber surfaces to a chemical state similar to their original chemical state, thereby restoring their pristine surface activity and surface functionality, for the next etching process. As a result, the etching processes performed in the treated chamber 30 yield more reproducible results, as compared to chambers where a wet cleaning or an RIE cleaning process is used to clean the chamber.

Preferably, the flow rate  $F_R$  of the cleaning gas and the power level  $P_L$  of the current applied to the gas activator 175, such as the microwave plasma generator 185, are selected to vaporize the etch residue on the etching chamber surfaces to a sufficiently low concentration to remove their effect on the chamber gas composition and substrate contamination, without eroding the walls or components in the chamber 30. The flow rate  $F_R$  of the cleaning gas should be sufficiently high to react with substantially all the etch residue on the ceramic surfaces to form gaseous byproducts. However, excessively high flow rates can cause erosion of the chamber walls and surfaces by the extended exposure to the highly activated gaseous species in the cleaning gas.

For example, it has been discovered that when etching silicon-containing layers on the substrate 25, a relatively thin etch residue containing primarily polymeric and silicon-containing species, and having a thickness of about 0.01 to about 1000 microns is formed on the chamber walls 45, 50, 55 and surfaces. This etch residue layer is removed by introducing into the chamber 30, an activated cleaning gas at a flow rate  $F_R$  equivalent to a rate of about 200 to about 2000 sccm for a chamber having a volume of about 40,000  $cm^3$  for a time period of about 0.5 to 100 seconds to clean the etch residue, substantially without eroding the walls and components in the chamber. For

different sized process chambers, equivalent flow rates of cleaning gas compositions that maintain substantially the same ratio of  $\text{NF}_3$  flow in sccm to chamber volume in  $\text{cm}^3$  should be used. While process gas consisting only of  $\text{NF}_3$  provides good results, inert gases such as helium or argon can also be added to the process gas, or the process gas can comprise a commercially available mixture of gases, such as  $\text{He-O}_2$ .

When a gas activator 175 which comprises a microwave generator 185 is used, the power level  $P_L$  operating the microwave generator 185, which is also a measure of the power or intensity of microwaves applied to the remote plasma chamber 40 via the gas activator 175, is selected to clean and treat the chamber 30 surfaces without eroding the chamber walls. The power level should be sufficiently high to provide a cleaning gas that is sufficiently reactive to remove substantially all the etch residue on the chamber walls and components without damage to the underlying structures. An excessively high power level  $P_L$  will cause the highly activated gaseous species to erode the chamber walls. Conversely, a cleaning gas activated at a power level that is too low, will fail to remove the thick chemically hard etch residue on portions of the chamber walls and components. Suitable power levels for the  $\text{NF}_3$  cleaning gas are from about 500 to about 4000 watts, and more preferably, from about 1500 to about 2500.

The activated gaseous species are introduced into the etching chamber 30 for a short burst of time to treat and condition the chamber. The short burst of activated cleaning gas provides significant advantages over conventional cleaning processes. First, the burst of activated cleaning gas provides a larger number of highly dissociated species that removes the etch residues, and cleans and conditions the ceramic surfaces in the chamber 30 by a "soft" chemically reactive process performed by the highly chemically reactive dissociated species. The burst and quick removal of the cleaning gas from the

chamber 30 also reduces the possibility of dissociated species from recombining to form other chemical species that erode the chamber surfaces and components. This mechanism is further aided by the high flow rates of the burst of gas which assist in flushing out the reaction byproducts before they recombine in the chamber 30. Also, the burst of gas maintains a fresh supply of cleaning gas at the exposed surfaces of the etch residue during the cleaning operation thereby removing the residue layers at a fast rate. Preferably, the burst of activated cleaning gas is introduced into the etching chamber at a flow rate  $F_R$  equivalent to a rate of at least about 200 to about 2000 sccm for an etching chamber 30 having a volume of about 40,000 cm<sup>3</sup> for a time period of about 0.5 to about 100 seconds to clean the etch residue, substantially without eroding the walls and components in the chamber. More preferably, the remotely generated cleaning gas is introduced into the etching chamber for about 0.5 to about 24 seconds.

In another aspect of the present invention, useful for reducing equipment down time and increasing throughput of the etching chamber 30, the cleaning process is performed while transporting the substrate 25 out of the chamber, or immediately after the substrate 25 is removed from the etching chamber 30. In this version, activated cleaning gas is prepared in the remote chamber 40, and while simultaneously transporting the substrate 25 out of the etching chamber 30, a burst of high flow rate  $F_R$  of activated cleaning gas is introduced into the etching chamber 30 for a time period sufficient to treat and condition the surfaces of the etching chamber 30 substantially without eroding the surfaces. For example, as the substrate 25 is finishing etching, the cleaning gas is introduced into the remote chamber 40 by opening an inlet valve 205 in the gas line between the cleaning gas supply 200 and the remote chamber 40; and the activated cleaning gas is allowed to flow into the etching chamber 30 while the substrate is being removed from the etching chamber 30. Inlet valve 205 of the remote chamber is in a closed position during etching of the

substrate, and as the etched substrate 25 is being removed or transported from the etching chamber 30, for example, while the substrate 25 is passing through the slit valve at the sidewall 45 of the etching chamber, a robot controller 259 sends a first signal that opens the inlet valve 205 to allow cleaning gas to enter into the remote chamber 40. For example, the robot controller 259 can provide a first trigger signal to the computer control system 230 that in response opens the inlet valve 205 and actuates the microwave generator 185, forming activated cleaning gas. The cleaning gas flows into the etching chamber 30 for a short time period to clean and condition the surfaces in the chamber 30. The robot controller 259 then provides a second trigger signal that closes the inlet valve 205 when a second substrate 25 is retrieved for insertion into the etching chamber 30 and allows the exhaust system 90 to exhaust residual activated gas from the etching chamber. Thereafter, another substrate 25 is transported into the chamber 30 and the etching, transportation, and chamber cleaning and conditioning steps are repeated, until all substrates 25 supply have been processed. In this method, the etching process stages are not delayed or slowed down by the cleaning process stages, thereby providing improved processing throughput.

In yet another version, an outlet valve 225 from the remote chamber is in a closed position during activation of the cleaning gas. As the etched substrate 25 is removed or transported from the etching chamber 30, the robot controller 259 sends a first signal that opens the outlet valve 225 in the gas conduit 170 allowing activated cleaning gas to flow into the etching chamber 30 for a short time period to clean and condition the surfaces in the chamber. The robot controller 259 then provides a second trigger signal that closes the outlet valve 225 when a second substrate 25 is retrieved for insertion into the etching chamber 30. Thereafter, another substrate 25 is transported into the chamber 30 and the etching, transportation, and chamber cleaning and conditioning steps are repeated.

In yet another aspect of the present invention, a lower pressure of gas is maintained in the etching chamber 30 relative to the pressure in the remote chamber 40. This aspect of the present invention can be used in conjunction with the specialized gas distributor structures described above to

5 direct the flow of cleaning gas adjacent to particular chamber surfaces that need to be cleaned more vigorously, for example, by providing the cleaning gas injection nozzles 235 adjacent to, or facing the portions of chamber having thicker etchant residues. It is believed that a more rapid flow of activated cleaning gas enters into the process chamber because of the differential

10 pressure maintained between the two chambers, causing the cleaning gas to rapidly impinge against and clean the chamber surfaces. In this process, the interior volume of the etching chamber 30 is maintained at a higher pressure than the remote chamber 40. In this method, the etching chamber 30 is preferably maintained at a lower pressure than the remote chamber 40. The

15 etching chamber 30 is preferably maintained at a pressure of 0.1 to 80 mTorr, and the remote chamber 40 is maintained at a pressure of about 500 to about 3000 mTorr.

In another preferred aspect of the invention, useful for cleaning

20 and conditioning chamber surfaces that are highly reactive to the etch residue, such as the ceramic surfaces, a multicycle cleaning process is used to treat chamber surfaces and reduce the concentration of etch residue. In a first stage, a first activated cleaning gas is formed by maintaining the gas activator 175, such as the microwave generator 185, at a first power level. In at least one

25 second stage, a second activated cleaning gas is formed by maintaining the gas activator 175 at a second power level that is lower than the first power level. The cleaning gas activated by the first higher power level of the first cleaning stage provides a more dissociated and chemically reactive species that removes the hard and thick etch residues on portions of the chamber walls 45, 50, 55

30 and components that are near the substrate 25. The cleaning gas in the second

cleaning stage is activated at a lower power level to efficiently treat and condition surfaces such as the ceramic surfaces, to provide optimal etching conditions in the chamber 30. Preferably, the first power level is at least about 500 watts, and more preferably from about 500 to about 3000 watts; and the  
5 second power level is at least about 1000 watts, and more preferably about 1500 to about 4000 watts. The multiple power level process is repeated a sufficient number of times to treat the chamber walls to reduce the concentration of etch residue in the chamber 30 to the desirable level, typically from a single cycle, to a range of about 1 to about 10 cycles. The duration of  
10 each cleaning stage is from about 0.5 to about 100 seconds, and more preferably, from about 2 to about 30 seconds.

The chamber treatment process of the present invention is advantageous because it maximizes the chemical reactivity of the activated  
15 cleaning gas to the etch residues in the chamber 30, and minimizes the chemical reactivity of the cleaning gas to the exposed surfaces in the etching chamber 30. The cleaning process has been found to uniformly remove etch residues, irrespective of their thickness or chemical stoichiometry. Prior art cleaning  
20 processes, particularly those performed by an operator, often fail to uniformly clean and remove the etch residue deposits formed on chamber surfaces. Build-up of etchant deposits on the chamber surfaces, result in flaking off the etchant deposits and contamination of the substrate 25 etched in the chamber. By uniformly removing the etch residues formed across substantially all of the chamber surfaces, such contamination and reduced yields from the substrate  
25 25, are minimized.

The activated cleaning gas also results in far less erosive damage to the chamber compared to conventional in-situ plasma cleaning steps, because of the reduced energy levels of the plasma in the etching chamber. This was  
30 difficult to accomplish in prior art processes, in which the high powered plasmas



used to remove the residue deposits also resulted in extensive erosion of chamber surfaces and components. By reducing the need to replace chamber components, the cost of operating the etching chamber 30 and the cost per substrate 25 are significantly reduced. Furthermore, the activated cleaning gas can be used to efficiently clean an etch chamber 30 in-situ during etching of substrates 25, and preferably during transport of the substrates between the etching chamber 30 and the loading chamber, rather than stopping processing in the chamber 30 to wet clean the chamber walls and components, thereby increasing etching throughput and further reducing costs per substrate. The cleaning process is expected to increase chamber lifetimes by a factor of at least 2, and also increase substrate yields by reducing the deposition of flaked-off etchant byproducts onto the substrate.

The treatment and cleaning process removes chemically-adhered etchant deposits from active surfaces in the chamber 30, and restores the original chemical reactivity and surface functional groups of these surfaces. The cleaning and treatment process is also particularly useful for cleaning etch residue that is strongly adhered to, or chemically reacted with ceramic surfaces, such as surfaces comprising one or more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide. The activated cleaning gas is effective at treating and reconditioning these ceramic surfaces to provide surface chemistries and surface functional groups that are chemically compatible with the etching process. The conditioned ceramic surfaces provide more reproducible etching properties in the chamber 30, than that provided by alternative chamber cleaning processes, such as wet cleaning or RIE cleaning processes. The significantly improved reproducibility of etching processes performed in the chamber 30 is highly desirable.

The present invention has been described with reference to certain preferred versions thereof; however, other versions are possible. For example, the treatment and cleaning process of the present invention can be used for treating chambers for other applications, as would be apparent to one of  
5 ordinary skill. For example, the process can be applied, as would be apparent to one of ordinary skill in the art, to treat sputtering chambers, ion implantation chambers, or deposition chambers, or in combination with other cleaning processes. Therefore, the spirit and scope of the appended claims should not be limited to the description of the preferred versions contained herein.

What is claimed is:

1. A method of cleaning an etch residue from walls and components of an etching chamber, the method comprising the steps of:
  - 5 (a) introducing a cleaning gas into a remote chamber adjacent to the etching chamber;
  - (b) activating the cleaning gas inside the remote chamber to form an activated cleaning gas; and
  - (c) introducing the activated cleaning gas into the
- 10 etching chamber to clean the etch residue on the walls and components of the etching chamber.
2. A method according to claim 1 wherein the etch residue comprises a layer containing polymeric and silicon-containing species, and
- 15 having a thickness of about 0.01 to about 1 micron, and  
wherein the activated cleaning gas is introduced into the etching chamber at a flow rate  $F_R$  equivalent to a rate of about 200 to about 2000 sccm for a chamber having a volume of about 40,000 cm<sup>3</sup> for a time period of about 0.5 to about 100 seconds.
- 20 3. A method according to claim 1 wherein the activated cleaning gas is introduced into the etching chamber for about 0.5 to about 24 seconds.
- 25 4. A method according to claim 2 wherein the cleaning gas is activated by microwaves applied in the remote chamber by a microwave plasma generator operated at a power level of about 500 to about 4000 Watts.
- 30 5. A method according to claim 1 wherein the etching chamber is maintained at a lower pressure than the remote chamber.

6. A method according to claim 8 wherein the etching chamber is maintained at a pressure of about 0.1 to about 80 mTorr, and the remote chamber is maintained at a pressure of about 500 to about 3000 mTorr.

5 7. A method according to claim 1 wherein the cleaning gas is selected from the group consisting of  $\text{NF}_3$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{C}_2\text{F}_6$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ , and mixtures thereof.

10 8. A method according to claim 1 wherein the surfaces in the etching chamber comprise one or more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide.

15 9. A method according to claim 1 comprising the initial step of etching silicon-containing layers on a substrate in the etching chamber, by the steps of:

- (a) introducing process gas comprising silicon etching gas into the etching chamber; and
  - (b) forming an etching plasma from the process gas by
- 20 applying RF current at a source power level to an inductor coil adjacent to the chamber, and applying a RF voltage at a bias power level to process electrodes in the chamber, wherein the power ratio  $P_s$  of the source power level to the bias power level is less than about 20:1, thereby rapidly etching the silicon-containing layer with reduced formation of etch residue on the walls and
- 25 components of the chamber.

10. A method of etching a substrate, and treating and conditioning surfaces of walls and components in an etching chamber, the method comprising the steps of:

- 5 (a) etching the substrate in the etching chamber thereby depositing etch residue on the surfaces of the walls and components in the etching chamber; and
- (b) simultaneously transporting the substrate out of the chamber, while introducing a burst of high flow rate  $F_R$  of activated cleaning gas into the etching chamber for a time period sufficient to treat and condition the
- 10 surfaces of the etching chamber substantially without eroding the surfaces.

11. A method according to claim 10 wherein in step (b) the activated cleaning gas is introduced into the etching chamber at a flow rate  $F_R$  equivalent to a rate of about 200 to about 2000 sccm for a chamber having a
- 15 volume of about 40,000 cm<sup>3</sup> for a time period of about 0.5 to about 100 seconds.

12. A method according to claim 11 wherein the activated cleaning gas is introduced into the etching chamber for about 0.5 to about 24
- 20 seconds.

13. A method according to claim 10 wherein the cleaning gas is activated by microwaves applied in the remote chamber by a microwave plasma generator operated at a power level of about 500 to about 4000 Watts.
- 25

14. A method according to claim 1 wherein the etching chamber is maintained at a higher pressure than the remote chamber.

15. A method according to claim 14 wherein the etching chamber is maintained at a pressure of about 0.1 to about 80 mTorr, and the remote chamber is maintained at a pressure of about 500 to about 3000 mTorr.

5           16. A method according to claim 11 wherein the surfaces in the etching chamber comprise one or more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide.

10           17. A method for treating an etching chamber to remove an etch residue from walls and components of the etching chamber, the method comprising the steps of introducing a burst of activated cleaning gas into the etching chamber at a flow rate  $F_R$  equivalent to a rate of at least about 200 to about 2000 sccm for an etching chamber having a volume of about 40,000 cm<sup>3</sup>  
15 for a time period of about 0.5 to about 100 seconds to clean the etch residue, substantially without eroding the walls and components in the chamber.

          18. A method according to claim 17 wherein the activated cleaning gas is introduced into the etching chamber for about 0.5 to about 24  
20 seconds.

          19. A method according to claim 17 wherein the cleaning gas is activated by microwaves applied in the remote chamber by a microwave plasma generator operated at a power level of about 500 to about 4000 Watts.

25           20. A method according to claim 17 wherein the etching chamber is maintained at a higher pressure than the remote chamber.

21. A method according to claim 20 wherein the etching chamber is maintained at a pressure of about 0.1 to about 80 mTorr, and the remote chamber is maintained at a pressure of about 500 to about 3000 mTorr.

5           22. A method according to claim 17 wherein the surfaces in the etching chamber comprise one or more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide.

10           23. A method for treating an etching chamber to remove an etch residue from walls and components of the etching chamber, the method comprising the steps of:

            (a) a first stage, in which a first activated cleaning gas formed by maintaining the gas activator in the remote chamber at a first power level, is introduced into the etching chamber;

15

            (b) at least one second stage, in which a second activated cleaning gas formed by maintaining the gas activator in the remote chamber at a second power level different from the first power level, is introduced into the etching chamber.

20

24. A method according to claim 23 wherein the first and second stages are each performed for about 0.5 to about 100 seconds.

25           25. A method according to claim 23 wherein in the first stage, the power level applied to the microwave generator is at least about 2000 watts, and wherein in the second stage, the power level applied to the microwave generator is at less than about 1000 watts.

26. A method according to claim 23 wherein in one or both of the stages, the activated cleaning gas is introduced into the etching chamber at a flow rate  $F_R$  equivalent to a rate of about 200 to about 2000 sccm for a chamber having a volume of about 40,000 cm<sup>3</sup>.

5

27. A method according to claim 23 wherein the etching chamber is maintained at a pressure of about 0.1 to about 80 mTorr, and the remote chamber is maintained at a pressure of about 500 to about 3000 mTorr.

10

28. A method according to claim 23 wherein the surfaces in the etching chamber comprise one or more of aluminum nitride, boron carbide, boron nitride, diamond, silicon oxide, silicon carbide, silicon nitride, titanium oxide, titanium carbide, yttrium oxide, and zirconium oxide.

15

29. An apparatus for etching a substrate, the apparatus comprising:

(a) an etching chamber having a process gas inlet for introducing process gas into the chamber, a plasma generator for forming a plasma from the process gas for etching a substrate, and an exhaust system for exhausting the spent process gas from the etching chamber;

20

(b) a remote chamber adjacent to the etching chamber for forming an activated cleaning gas therein;

(c) a gas distribution system comprising (i) a gas conduit for transporting the activated cleaning gas from the remote chamber to the etching chamber, (ii) a gas flow distributor for directing the flow of activated cleaning gas substantially parallel, and adjacent to, one or more internal surfaces of the chamber, and (iii) a gas flow regulator for regulating the flow of activated cleaning gas into the gas flow distributor.

25



30. The apparatus of claim 29 wherein the gas flow distributor comprises a plurality of gas injection nozzles positioned in the etching chamber to be adjacent to the portions of the surfaces in the chamber that have thicker etch residue layers.

5

31. The apparatus of claim 29 wherein the gas flow distributor comprises a plurality of gas injection nozzles arranged symmetrically about a central axis of the chamber.

10

32. The apparatus of claim 29 wherein the gas flow injection nozzles are positioned behind a plate parallel to a surface of the chamber.

15

33. The apparatus of claim 29 wherein the gas flow distributor comprises one or more gas injection nozzles terminating in a channel in the chamber, the channel comprising an extended annular ledge covering at least a portion of the channel.

20

34. A method of using the apparatus of claim 29 to etch a substrate, the method comprising the steps of:

- (1) etching the substrate in the etching chamber;
- (2) removing the substrate from the chamber; and
- (3) during or after step (2), cleaning and conditioning the chamber by introducing activated cleaning gas into the etching chamber using the gas flow distribution system.

25

35. An apparatus for etching a substrate, the apparatus comprising:

- (a) an etching chamber having a process gas inlet for introducing process gas into the chamber, a plasma generator for forming a

plasma from the process gas for etching a substrate, and an exhaust system for exhausting the spent process gas from the etching chamber;

(b) a remote chamber adjacent to the etching chamber for forming an activated cleaning gas therein;

5 (c) a gas distribution system comprising (i) a gas conduit for transporting the activated cleaning gas from the remote chamber to the etching chamber, (ii) a gas flow distributor having nozzles positioned adjacent to a surfaces in the chamber that have thicker etch deposit layers, for directing the flow of activated cleaning gas to these regions to preferentially remove the  
10 thicker etch deposit layers without eroding portions of the chamber having thinner deposit layers.

36. The apparatus of claim 35 wherein the gas flow distributor comprises a plurality of gas injection nozzles arranged symmetrically about a  
15 central axis of the chamber.

37. The apparatus of claim 35 wherein the gas flow injection nozzles are positioned behind a plate parallel to a surface of the chamber.

20 38. The apparatus of claim 35 wherein the gas flow distributor comprises one or more gas injection nozzles terminating in a channel in the chamber, the channel comprising an extended annular ledge covering at least a portion of the channel.

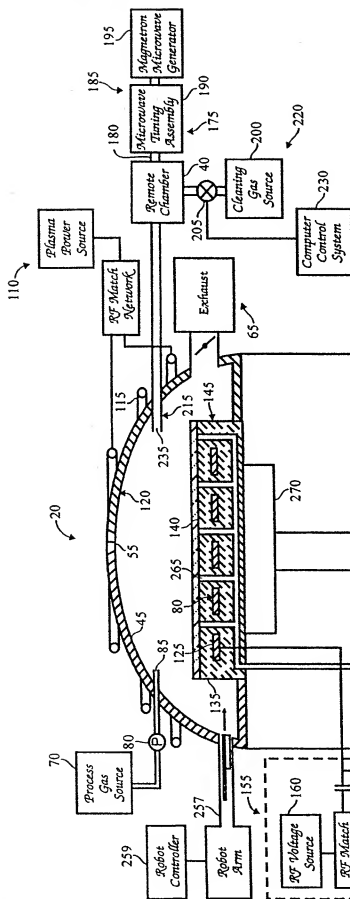
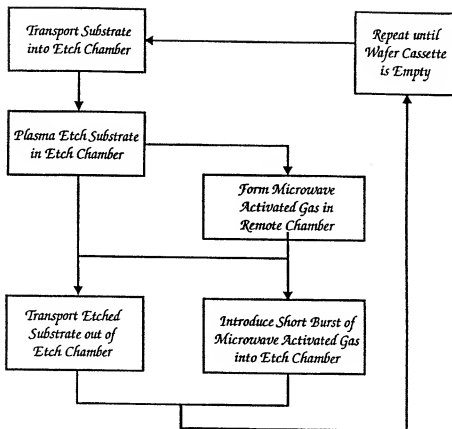


Fig. 1

*Fig. 2*

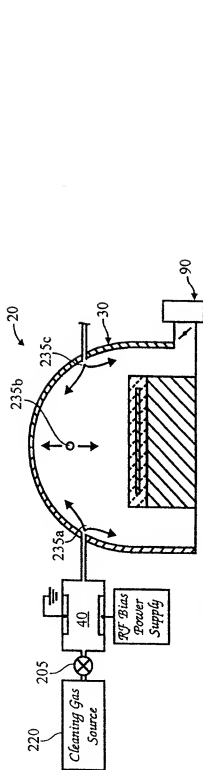


Fig. 3

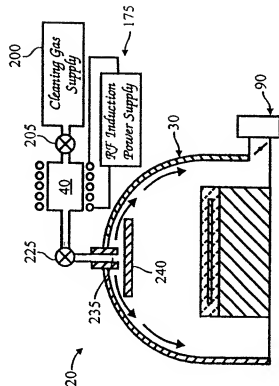


Fig. 4

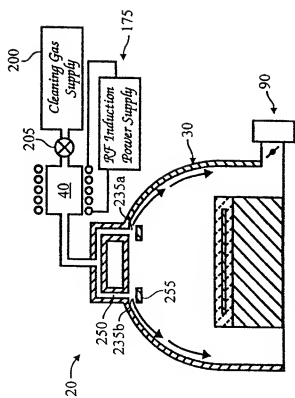


Fig. 5

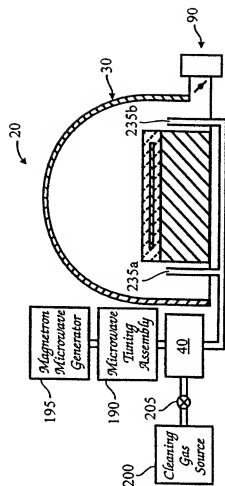


Fig. 6

# INTERNATIONAL SEARCH REPORT

International Application No.  
PC1/JS 98/21806

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C23C16/44

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C H01J B08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 224 (E-525), 21 July 1987 & JP 62 040728 A (TOKUDA SEISAKUSHO LTD; OTHERS: 01), 21 February 1987	1,5,10, 14
Y	see abstract	34
X	US 5 389 197 A (ISHIMARU YASUSHI) 14 February 1995	29,35
Y	see column 4, line 48 - column 5, line 30; figure 2	34
A	US 5 637 237 A (OEHRLEIN GOTTLIEB S ET AL) 10 June 1997 see column 5, line 38 - line 44	8,16,22
A	EP 0 697 467 A (APPLIED MATERIALS INC) 21 February 1996 see claims 1-23	1-38
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"I" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

12 February 1999

Date of mailing of the international search report

18/02/1999

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patenlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Ekhult, H

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/US 98/21806

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 555 546 A (IBM) 18 August 1993 cited in the application see the whole document -----	1-38
A	DE 41 32 559 A (SIEMENS AG) 8 April 1993 cited in the application see the whole document -----	1-38
A	EP 0 790 635 A (NOVELLUS SYSTEMS INC) 20 August 1997 see claim 1; figure 1 -----	29-31



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21806

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5389197 A	14-02-1995	JP 5206069 A	13-08-1993
US 5637237 A	10-06-1997	US 5798016 A	25-08-1998
		DE 19506745 A	14-09-1995
		JP 8037180 A	06-02-1996
EP 0697467 A	21-02-1996	JP 9069504 A	11-03-1997
EP 0555546 A	18-08-1993	US 5443686 A	22-08-1995
DE 4132559 A	08-04-1993	JP 5214531 A	24-08-1993
EP 0790635 A	20-08-1997	DE 790635 T	12-03-1998
		JP 9249976 A	22-09-1997



US 20050139578A1

(19) **United States**(12) **Patent Application Publication**

Fukuda et al.

(10) Pub. No.: **US 2005/0139578 A1**

(43) Pub. Date:

**Jun. 30, 2005**(54) **THIN-FILM FORMING APPARATUS HAVING  
AN AUTOMATIC CLEANING FUNCTION  
FOR CLEANING THE INSIDE**(75) Inventors: **Hideaki Fukuda, Tokyo (JP); Kiyoshi  
Sato, Tokyo (JP)****Related U.S. Application Data**(62) Division of application No. 09/511,934, filed on Feb.  
24, 2000, now abandoned.**Publication Classification**(51) Int. Cl.<sup>7</sup> ..... C23F 1/00

(52) U.S. CL ..... 216/67; 156/345.35

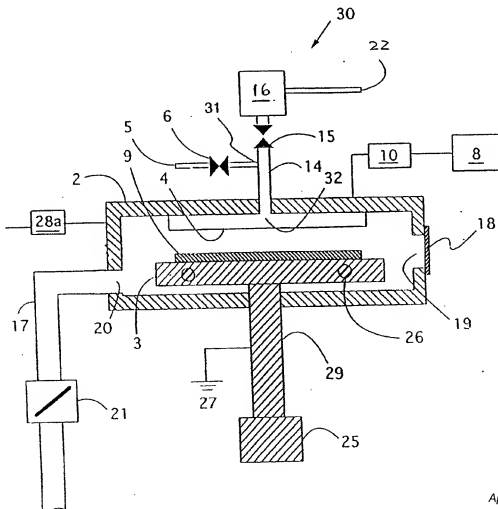
(57)

**ABSTRACT**

A method of cleaning the inside of a reaction chamber includes reducing the temperature of a susceptor to 470° C. or lower for cleaning; contacting the inside of the reaction chamber including the showerhead with fluorine radicals; cleaning the unwanted deposits by the fluorine radicals, wherein gaseous aluminum fluoride is inhibited from being emitted from the susceptor and solidified on the showerhead by maintaining the temperature of the susceptor at 470° C. or lower; and raising the temperature of the susceptor to 500-650° C. for film formation.

Correspondence Address:

**KNOBBE MARTENS OLSON & BEAR LLP  
2040 MAIN STREET  
FOURTEENTH FLOOR  
IRVINE, CA 92614 (US)**

(73) Assignee: **ASM JAPAN K.K., Tokyo (JP)**(21) Appl. No.: **11/068,089**(22) Filed: **Feb. 28, 2005****APPENDIX B**

Appl. No.: 10/759,953



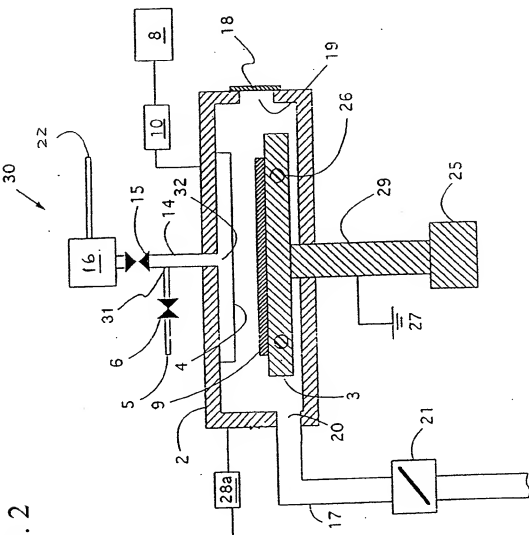


FIG. 2

FIG. 3

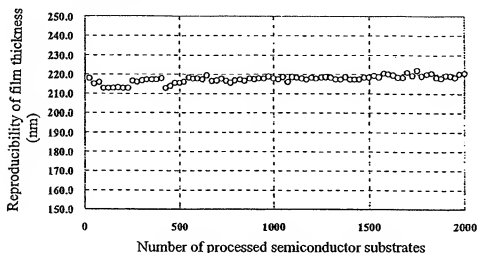


FIG. 4

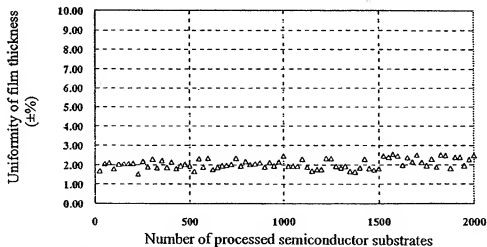
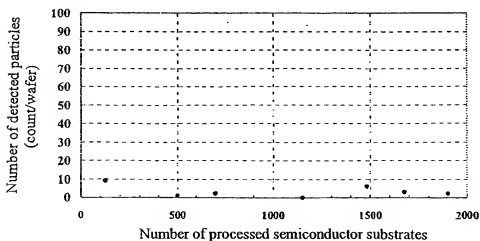


FIG. 5



# THIN-FILM FORMING APPARATUS HAVING AN AUTOMATIC CLEANING FUNCTION FOR CLEANING THE INSIDE

[0001] This application is a divisional of U.S. patent application Ser. No. 09/511,934, filed Feb. 24, 2000, the disclosure of which is incorporated herein by reference in its entirety.

## BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates to a thin-film forming apparatus that is used in a process for semiconductor device circuit manufacturing, and particularly to a thin-film forming apparatus having an automatic cleaning function, and an automatic cleaning method of a thin-film forming apparatus.

[0004] 2. Description of the Related Art

[0005] In the process of forming a film on a semiconductor substrate, the semiconductor substrate, i.e., workpiece is placed on a resistance type of heater that functions as a susceptor provided in an evacuated reaction chamber. After a showerhead having holes for expelling reaction gas is opposed to the heater, radiofrequency energy at 13.56 MHz is applied to the showerhead, by which a plasma discharge region is formed between the heater supporting the semiconductor substrate and the showerhead. Reaction gas supplied by the showerhead is excited and activated in the plasma discharge region, and a film is formed, depending on the kinds of reaction gas, on the semiconductor substrate. At this time, films and reaction by-products adhere to the inside surface of the reaction chamber in addition to the semiconductor substrate.

[0006] With repeated film formation processes, unwanted deposits adhering to portions other than the semiconductor substrate accumulate. After separating from the attached surface the unwanted deposits become particles and stick to the surface of the semiconductor substrate, causing impurity contamination, stopping functions of semiconductor devices. To eliminate unwanted deposits from the reaction chamber, many thin-film-forming apparatuses may have an automatic cleaning function.

[0007] The automatic cleaning function cleans the reaction chamber using a fluorine-containing active species, after detaching the semiconductor substrate on which film formation is complete, from the heater and conveying it outside of the reaction chamber. Specifically, when forming a silicon nitride film on the semiconductor substrate, a mixture gas of  $\text{SiH}_4$ ,  $\text{NH}_3$  and  $\text{N}_2$  is furnished to the reaction chamber as a reaction gas to produce a plasma discharge region in the reaction chamber using radiofrequency energy.

[0008] The unwanted deposits, which mainly comprises the same material as the film deposited on a semiconductor substrate, also adhere to the inner surface of the reaction chamber. After the finished semiconductor substrate is conveyed outside of the reaction chamber,  $\text{C}_2\text{F}_6$  and oxygen or a mixture gas of  $\text{C}_3\text{F}_8$  and oxygen are supplied to the reaction chamber from the showerhead. Then fluorine active species is generated in the reaction chamber by applying radiofrequency energy of 13.56 MHz. The unwanted deposits inside of the reaction chamber are gasified by the fluorine active species and exhausted from the reaction chamber.

Automatic cleaning sequence after performing film formation once or more than once on the semiconductor substrate always keeps clean the inside of the reaction chamber.

[0009] Film-forming requirements of a silicon nitride film and a silicon oxinitride film (silicon nitride type of film) by a capacitance coupling plasma CVD method are conventionally that a gas flow ratio of a  $\text{SiH}_4\text{:N}_2\text{:NH}_3$  system is approximately  $\text{SiH}_4\text{:N}_2\text{:NH}_3=1\text{:}1\text{:}50\text{--}1\text{:}10$ , and that the temperature for a workpiece is approximately below  $400^\circ\text{C}$ . Both requirements are used industrially for insulating films of a semiconductor device. Some examples of the film-forming requirements are disclosed in U.S. Pat. No. 5,336,640. Since the films incorporate hydrogen, when a step having a higher temperature than the film-forming temperature follows, the hydrogen incorporated in the films is released, which remarkably worsens electrical characteristics of the semiconductor device. Therefore, a main application is a final passivation film for the semiconductor device which does not have the step of higher temperature processing (the example disclosed in U.S. Pat. 5,336,640 is the one used as a final protection film).

[0010] To solve a problem of an increase in RC delay (which is proportional to the product of metal line resistance and capacitance between lines) in the wiring accompanied by increased density of semiconductor devices, there are proposals that resistance should be lowered by the introduction of Cu wiring, and that distribution line capacitance should be reduced. In the semiconductor device having Cu wiring, because the Cu wiring is high in heat resistance, a SiOF film formed by relatively high temperature plasma CVD can be used as an insulating film disposed between the metal lines.

[0011] When applying Cu wiring, a damascene step is generally conducted in which ditch patterns of metal lines in an insulating film between layers are formed and Cu wiring is embedded in the ditches. To form the ditches in an insulating film between layers, hetero-etching by reactive ion etching (RIE) can be used. A silicon nitride type of film formed by plasma CVD may be used as a RIE etching-stopping layer. A silicon nitride type of film formed by plasma CVD may be used as an antireflective film to prevent the reflection of exposed light in the lower part of a resist at a lithography step so as to accurately perform a fine-structure processing.

[0012] In the above situations, a processing temperature of approximately  $400^\circ\text{C}$ . has increased to exceed  $500^\circ\text{C}$ . When the substrate is heated to over  $500^\circ\text{C}$ . and film-forming on the semiconductor substrate is executed, unwanted deposits adhere to the inside of the reaction chamber. Since the attached unwanted deposits are a source of particles and contamination, they are removed by executing the automatic cleaning sequence as previously mentioned. In the process of forming a silicon nitride film, gas including fluorine is used for automatic cleaning. At the plasma discharge region in the reaction chamber or at the excitation chamber isolated from the reaction chamber, a fluorine active species is generated which is used to remove the unwanted deposits in the reaction chamber. In order to form a film on the semiconductor substrate, the surface of the ceramic heater supporting the substrate is set at a predetermined temperature range for film formation. When the semiconductor substrate on which film formation is

complete is conveyed out of the reaction chamber, the automatic cleaning sequence follows immediately. That is, parts in the reaction chamber, especially a ceramic heater which holds directly and heats a semiconductor substrate, is in a state so-called "film-forming temperature" at which high temperature it is exposed to the environment of automatic cleaning. However, the above conventional cleaning treatment causes problems as described below.

#### SUMMARY OF THE INVENTION

[0013] In order to form a film on the semiconductor substrate, the surface of the ceramic heater supporting the substrate is set at a predetermined temperature range of 470°-600° C. In the temperature environment in excess of 470° C., even aluminum nitride reacts with the fluorine active species to generate aluminum fluoride, which in turn emits the aluminum fluoride generated to the reaction chamber. When the surface temperature of the heater exceeds 500° C., generation and emission of aluminum fluoride causes extensive damage to the reaction chamber. The temperature of the surface of a showerhead opposed to the ceramic heater supporting the semiconductor substrate is 100-250° C. which is lower than that of the ceramic heater. Aluminum fluoride emitted from the ceramic heater adheres to the showerhead of relatively lower temperature, and accumulates due to the reaction with fluorine active species during the automatic cleaning sequence. The aluminum fluoride once stuck to the showerhead cannot be removed except for wiping off with the reaction chamber open.

[0014] An objective of the present invention is to provide an automatic cleaning method which does not produce aluminum fluoride on a showerhead.

[0015] Another objective of the present invention is to realize forming a film with good reproducibility and without foreign contamination (particles) by an automatic cleaning sequence.

[0016] Yet another objective of the present invention is to provide a thin-film forming apparatus which reduces non-working hours for cleaning and enhances productivity by use of an automatic cleaning sequence.

[0017] Namely, an embodiment of the present invention A thin-film forming apparatus comprising: (a) a reaction chamber for forming a thin film on a workpiece placed on a susceptor provided in the reaction chamber, which susceptor is provided with a heater for heating the workpiece, which reaction chamber is provided with a conveyor for loading and unloading the workpiece into and from the reaction chamber; and (b) a cleaning device for cleaning unwanted deposits adhering to the inside of the reaction chamber at predetermined intervals, which cleaning device comprises: (i) a cleaning gas controller for introducing a cleaning gas into the reaction chamber and evacuating the reaction chamber after the cleaning treatment; (ii) a cleaning gas activator for activating the cleaning gas in radical form; and (iii) a temperature and timing controller programmed to reduce the temperature of the susceptor at a predetermined rate for cleaning after completion of film formation and then to actuate the cleaning gas controller and the cleaning gas activator.

[0018] In the above, the temperature of the susceptor for cleaning is preferably 500° C. or less, more preferably 470°

C. or less, while the temperature of the susceptor for film formation may be higher than 500° C. In an embodiment, the cleaning gas includes fluorine, and the activated cleaning gas includes fluorine radicals. Among others, the cleaning gas can be activated using a plasma discharge region generated in the reaction chamber or using a remote plasma discharge chamber prior to introduction of the cleaning gas into the reaction chamber. Further, the cleaning gas controller can introduce the cleaning gas through a showerhead disposed above the susceptor in the reaction chamber.

[0019] In an embodiment, the unwanted deposits include silicon nitride, SiO, SiON, SiOF, SiC, and hydrocarbon. The apparatus includes a plasma CVD apparatus and a thermal CVD apparatus.

[0020] The present invention can also apply to a method for cleaning unwanted deposits adhering to the inside of a reaction chamber for forming a thin film on a workpiece placed on a susceptor provided in the reaction chamber, said susceptor being provided with a heater for heating the workpiece, said reaction chamber being provided with a conveyor for loading and unloading the workpiece into and from the reaction chamber, said method comprising: (a) reducing the temperature of the susceptor at a predetermined rate for cleaning after completion of film formation; (b) contacting the inside of the reaction chamber with an activated cleaning gas; and (c) cleaning the unwanted deposits by the activated cleaning gas.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 shows one example of a thin film-forming and processing apparatus according to the present invention.

[0022] FIG. 2 illustrates a thin film-forming and processing apparatus having a remote plasma discharge chamber.

[0023] FIG. 3 illustrates the measurement results of the thickness of formed silicon nitride films.

[0024] FIG. 4 illustrates the distribution lines of the thickness of formed silicon nitride films on one semiconductor substrate 9.

[0025] FIG. 5 illustrates the measurement results of particles on the surface of semiconductor substrates after the formation of silicon nitride films.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

##### [0026] Applicable Thin-Film Forming Apparatus

[0027] When a conventional silicon nitride film formed by plasma CVD in the semiconductor device is used, a problem arises. That is, after forming a silicon nitride type of film having a high hydrogen concentration which has been used as a final protection film in the past, when forming a SiOF film formed by relatively high temperature plasma CVD on the silicon nitride type of film, hydrogen in the SiOF film is dissociated during formation and coherence of the film is reduced, causing separation of the film. The reason is that the film-forming temperature is 470° C., which is relatively high. When separation of the film has occurred, yield of the workpiece will, as a whole, drop because a semiconductor device including separated portions causes short circuits in distribution lines and poor conduction.

[0028] A silicon nitride type of film formed by thermal CVD over 700° C. without plasma may not be used as an inter-layers insulating film, because the film-forming temperature is too high after formation of Al or Cu. Since almost no hydrogen is included in the film, the silicon nitride type of film has been used as an etching stopping layer for a first between-layers insulating film on the semiconductor device to which a thermal step is applied later.

[0029] However, because semiconductor devices have become highly minute in recent years, accordingly, gate length has become smaller and it is now below 0.18  $\mu\text{m}$ . Therefore it is difficult to prevent formation and diffusion of impurity layers due to the thermal load when in high temperature thermal steps of over 700° C. In the case of insufficient control of diffused layers, reliance on semiconductor devices will be reduced since there is produced dispersion in operating voltage. Thus, desired is a film-forming method requiring a low thermal load for semiconductor devices which enables film-forming at a lower temperature than that of high temperature thermal CVD, the film being a silicon nitride type of film having a low density of hydrogen.

[0030] To this end, the inventors have invented a method of forming a silicon nitride film using plasma CVD at a relatively higher temperature which is described in Japanese Patent Application No. 11-243914. By raising a semiconductor substrate temperature of approximately 400° C. in the past to a range of 430-600° C., a silicon nitride film having a low density of hydrogen can be formed. The semiconductor substrate temperature is preferably over 470° C. and more preferably over 550-600° C.

[0031] To set a semiconductor substrate temperature at 470-600° C., the surface of a heater (which supports the semiconductor substrate) for heating the substrate requires raising the temperature to 500-650° C., which is beyond the heat resistance of a metallic heater where a sheath heater is buried in conventional aluminum alloy. Accordingly, a ceramic heater is used so that high temperatures can be attained. As a ceramic material, aluminum nitride with high heat conductivity may generally be used. A ceramic heater comprising an aluminum nitride disk or plate has a resistance heater and a metal for a plasma-discharge ground electrode embedded by integral sintering, which allows the semiconductor substrate to be heated to approximately 650° C.

#### [0032] Analysis of Conventional Cleaning System

[0033] When the substrate is heated to over 470° C. using the ceramic heater and film-forming on the semiconductor substrate is executed, unwanted deposits adhere to the inside of the reaction chamber. Since the attached unwanted deposits are a source of particles and contamination, they are removed by executing the automatic cleaning sequence as previously mentioned. In the process of forming a silicon nitride film, gas including fluorine is used for automatic cleaning. At the plasma discharge region in the reaction chamber or at the excitation chamber remote from the reaction chamber, a fluorine active species is generated which is used to remove the unwanted deposits in the reaction chamber.

[0034] In order to form a film on the semiconductor substrate, the surface of the ceramic heater supporting the

substrate is set at a predetermined temperature range of 470-600° C. When the semiconductor substrate on which film formation is complete is conveyed out of the reaction chamber, the automatic cleaning sequence follows immediately. That is, one of the parts in the reaction chamber, especially a ceramic heater which holds directly and heats a semiconductor substrate, is in a state so-called "film-forming temperature" at which high temperature it is exposed to the environment of automatic cleaning. In the temperature environment in excess of 470° C., even aluminum nitride reacts with the fluorine active species to generate aluminum fluoride, which in turn emits the aluminum fluoride generated to the reaction chamber.

[0035] When the surface temperature of the heater exceeds 500° C., generation and emission of aluminum fluoride causes extensive damage to the reaction chamber. The temperature of the surface of a showerhead opposed to the ceramic heater supporting the semiconductor substrate is 100-250° C. which is lower than that of the ceramic heater. Aluminum fluoride emitted from the ceramic heater adheres to the showerhead of relatively lower temperature, and accumulates due to the reaction with fluorine active species during the automatic cleaning sequence. The aluminum fluoride once stuck to the showerhead cannot be removed except for wiping off with the reaction chamber open.

[0036] The accretion of aluminum fluoride to the surface of the showerhead causes two substantial problems. One problem is that growth speed of a film to be formed on the semiconductor substrate varies. When non-conductive aluminum fluoride adheres to the surface of the showerhead, the non-conductive aluminum fluoride functions as a newly formed electric insulator formed on the surface of the showerhead, thereby reducing a film-forming speed. The difference in accretion of aluminum fluoride (thickness) at the surface of the single showerhead produces abnormal distribution lines in formed film thickness on the surface of a semiconductor substrate. The degree of variability of no more than  $\pm 3\%$  is required regarding film thickness (value defined by subtracting the minimum thickness from the maximum thickness and dividing it by 2 times the average).

[0037] Differences in film thickness formed on the semiconductor substrate leads to non-uniformity of semiconductor device functions of the semiconductor substrate. In the case where film thickness cannot be attained as designed, the semiconductor devices do not function properly and are judged to be inferior. Attachment of aluminum fluoride to the entire surface of the showerhead gives rise to insufficient thickness of the entire film on the semiconductor substrate. Repeated film formation on the semiconductor substrate gradually reduces film thickness which should otherwise increase. According to present technological standards, reproducibility of film thickness on the semiconductor substrate should be less than approximately  $\pm 3\%$ . When film thickness grown on the semiconductor substrate varies beyond this value, all the semiconductor devices on the semiconductor substrate are inferior.

[0038] The second problem is contamination of the semiconductor substrate by particles. If aluminum fluoride accretes to and accumulates on the surface of the showerhead, particles of the aluminum fluoride will slough off the surface and adhere to the surface of the semiconductor substrate. The aluminum fluoride deposited on the semicon-



ductor substrate cause contamination or defect at the bottom, middle or surface of a film to be formed on the semiconductor substrate, which causes malfunctions of the semiconductor device. Generally speaking, the number of particles attached on the semiconductor substrate should not exceed 20 with a diameter of over 0.2  $\mu\text{m}$ .

[0039] In addition, in order to eliminate problems caused by aluminum fluoride, as mentioned before, there is no other way than to physically remove aluminum fluoride accreted to the surface of the showerhead; film-forming and processing is interrupted, the reaction chamber is opened, and wipe-off cleaning must be done manually. Because the wipe-off cleaning is performed while film-forming and processing by a thin-film forming apparatus are stopped, operating efficiency and productivity of the apparatus are remarkably decreased.

[0040] Film-Formation and Processing Prior to Cleaning

[0041] In an embodiment, there is provided a first semiconductor substrate as a workpiece for film-forming and processing, on a heater with a surface temperature of over 500° C. placed in a reaction chamber of a thin-film forming apparatus. Reaction gas is furnished from a showerhead to which is applied radiofrequency energy of 13.56 MHz. At a plasma discharge region generated between the showerhead and the heater supporting the semiconductor substrate, the reaction gas is dissolved and a thin film is formed on the semiconductor substrate. The first semiconductor substrate, on which film formation is complete, is removed from the heater and conveyed out of the reaction chamber. A second semiconductor substrate for film-forming and processing is carried into the reaction chamber and is placed on the heater. The same film-forming and processing steps are conducted as with the first semiconductor substrate. The second semiconductor substrate is removed from the reaction chamber after film-forming and processing is complete.

[0042] When conducting a series of film-forming and processing processes (film sequence) of #1 to #n semiconductor substrates, after removing the #n semiconductor substrate from the reaction chamber, a cleaning sequence follows which cleans unwanted deposits adhering to the inside of the reaction chamber.

[0043] Subsequent Cleaning Sequence

[0044] The cleaning sequence includes a cooling step which lowers the temperature of the heater supporting and heating the semiconductor substrate. When the #n semiconductor substrate is removed from the reaction chamber and automatic cleaning for the reaction chamber gets ready to operate, nitrogen gas is introduced into the reaction chamber to obtain an arbitrary pressure and the temperature of the ceramic heater is lowered at a rate not exceeding 20° C. per minute.

[0045] When the surface temperature of the ceramic heater is below 500° C., cleaning gas is injected into the reaction chamber to conduct automatic cleaning in the reaction chamber and unwanted deposits adhering to the inside of the reaction chamber will be gasified and exhausted. The cleaning step which removes the products from the reaction chamber can be performed substantially in the following way, although the step should not be limited thereto:

[0046] In-Situ Plasma Cleaning

[0047] In an embodiment, a mixture gas of  $\text{C}_2\text{F}_6$  gas and oxygen gas controlled at a predetermined flow is introduced,

as a cleaning gas, into the reaction chamber from the shower head. Maintaining the inside of the reaction chamber at a predetermined pressure, radiofrequency energy of 13.56 MHz, for example, is applied to the showerhead to form a plasma discharge region between the showerhead and the ceramic heater. The cleaning gas introduced from the showerhead is activated by the plasma discharge to become a fluorine-containing active species which reacts with the unwanted deposits adhering to the inside of the reaction chamber and transforming into gas material to be evacuated from the reaction chamber by an evacuation pump. During the cleaning step, the surface temperature of the ceramic heater is kept at below 500° C.

[0048] The cleaning step is terminated when radiofrequency energy applied to the showerhead and  $\text{C}_2\text{F}_6$  gas is terminated. The oxygen gas supplied to the reaction chamber as part of the cleaning gas is injected into the reaction chamber after the completion of the cleaning step. The fluorine active species produced during the cleaning step and the reaction products produced by the reaction between the fluorine active species and the unwanted deposits in the reaction chamber are purged from the reaction chamber. After evacuating the reaction chamber, a heating step follows that raises the temperature of the ceramic heater to the temperature for film-forming and processing of the semiconductor substrate. When the ceramic heater temperature reaches a predetermined temperature, the automatic cleaning sequence is complete. When the automatic cleaning sequence is finished, the #(n+1) semiconductor substrate is brought in the reaction chamber to be placed on the ceramic heater. Then the aforementioned thin film-forming and processing of the semiconductor substrate (film-forming sequence) is conducted.

[0049] Remote Plasma Cleaning

[0050] The aforementioned cleaning step can be done in another way including the following: The cleaning gas is activated in a remote plasma discharge chamber remote from the reaction chamber where thin film formation on the semiconductor substrate is performed. The activated cleaning gas is introduced via a duct into the reaction chamber where thin-film forming and processing to the semiconductor substrate is executed. The activated cleaning gas, introduced into the reaction chamber, transforms the unwanted deposits adhering to the inside of the reaction chamber into gaseous material which is expelled from the reaction chamber.

[0051] When thin film-forming and processing of a predetermined number of semiconductor substrates is complete and when the automatic cleaning sequence in the reaction chamber is complete, the cooling step is conducted which reduces the temperature of the heater supporting the semiconductor substrate to below 500° C. When the cooling step is complete, argon gas controlled at a predetermined flow rate is furnished in the remote plasma discharge chamber. After radiofrequency discharge of 400 kHz is generated in the remote plasma discharge chamber, a cleaning gas including fluorine such as  $\text{NF}_3$  controlled at a predetermined flow rate is introduced to generate a fluorine active species. The fluorine active species is introduced into the reaction chamber via the remote plasma discharge chamber and the duct

which connects the reaction chamber for film formation. The inside of the reaction chamber is cleaned by the fluorine active species, the heating step is performed as previously described wherein the heater temperature in the reaction chamber is raised to the thin film formation temperature.

[0052] The first automatic cleaning sequence mentioned is called in-situ plasma cleaning, in which, to activate cleaning gas, a discharge electrode in the reaction chamber used at the time of film formation and a radiofrequency energy supply are employed. The second automatic cleaning sequence mentioned is called remote plasma cleaning, in which, to activate cleaning gas, the remote plasma discharge chamber placed away from the reaction chamber is used, but not the radiofrequency energy supply for film formation.

#### EXAMPLE 1

[0053] Structures of Apparatus (In-Situ Plasma Cleaning)

[0054] FIG. 1 shows one example of a thin film-forming and processing apparatus 1 according to the present invention, in which a parallel plate plasma CVD apparatus and an in-situ plasma cleaning apparatus for automatic cleaning are used.

[0055] A workpiece 9 to be processed such as a semiconductor substrate is placed on a ceramic heater 3 to hold the workpiece in a reaction chamber 2. Opposed to the heater 3 is placed a showerhead 4 which provides uniform reaction gas on the workpiece 9. Reaction gas for forming a film on the surface of the workpiece 9 is controlled at a predetermined flow by a mass flow controller (not shown), and enters a duct 5 to a duct 11 through a valve 6. After passing through an aperture 7 of the reaction chamber 2, the gas is provided within the reaction chamber 2 through thousands of tiny holes, with a diameter of less than 1 mm, of the showerhead 4.

[0056] To evacuate the reaction chamber 2, an evacuation pump (not shown) is connected to an aperture 20 of the reaction chamber 2 via a duct 17 and a conductance-controlling valve 21. The heater 3 for holding the workpiece 9 includes an aluminum nitride plate 13 with a resistance heating element 26 embedded, and is connected to the reaction chamber 2 by a shaft 29.

[0057] Film-Formation Process

[0058] A method of forming a film on the workpiece 9 will be explained below. When a silicon nitride film is formed on the workpiece 9, gases of  $\text{SiH}_4$ ,  $\text{NH}_3$  and  $\text{N}_2$ , or  $\text{SiH}_4$  and  $\text{NH}_3$ , or  $\text{SiH}_4$  and  $\text{N}_2$  are used as a reaction gas, and radiofrequency energy of 13.56 MHz, or power of a mixture of 13.56 MHz and 430 kHz is applied to the showerhead 4. The workpiece 9 receives heat from the heater with 600° C. to have a temperature in the range of approximately 530° C.-550° C. Reaction gases such as  $\text{SiH}_4$  and  $\text{N}_2$ , etc. are introduced into the duct 11 through the valve 6 from the duct 5, and are uniformly supplied to the inside of the reaction chamber 2 through the shower head 4 from the aperture 7 of the duct 11. While introducing the reaction gases into the reaction chamber 2 at a predetermined flow rate, the pressure of the reaction chamber 2 is adjusted in a range of 1 Torr to 8 Torr in response to a signal at a pressure meter 28a via the opening of a conductance controlling valve 21 controlled by a pressure controller 28.

[0059] As mentioned above, while maintaining the temperature, gas flow and pressure controlled at predetermined values, a predetermined radiofrequency energy is applied between the electrodes to generate plasma, which in turn forms a silicon nitride film on the workpiece 9. By controlling the duration of time that the radiofrequency energy is applied, a silicon nitride film with a necessary thickness may be obtained. After completing formation of the film on the workpiece 9, the workpiece 9 is conveyed outside of the reaction chamber 2 by an automatic conveyor (not shown) when a gate valve 18 of a reaction chamber opening 19 is opened.

[0060] In-Situ Plasma Cleaning Sequence

[0061] The unwanted deposits adhering to the inside of the reaction chamber 2 in forming the film on the workpiece are removed in an automatic cleaning sequence. The automatic cleaning sequence comprises the steps of: cooling, which cools the temperature of the heater 3 supporting the workpiece 9 to below 500° C.; cleaning, which cleans the inside of the reaction chamber 2; and heating, which raises the temperature of the heater 3 to 600° C. for film formation.

[0062] In the cooling step, introducing nitrogen gas at 2 liters per minute (2 slm) in the reaction chamber 2, the pressure can be within a range of 0.5-9 Torr, and the temperature of the heater 3 can be lowered at a rate of not over 20° C. per minute. The flow of nitrogen gas is not limited to 2 liters per minute. The gas to be introduced is not limited to nitrogen; instead, inert gas, such as helium, argon, etc. which do not damage the ceramic heater 3, the reaction chamber 2, and the articles inside, may be used. The temperature lowering rate of the heater 3 is not limited to under 20° C. per minute; any rate which does not cause damage to the heater 3 may be used. When the temperature of the heater 3 is below 500° C., the cooling step is complete. Preferably, it should be below 450° C. The temperature of the heater 3 is defined by that on the surface of the ceramic heater which touches the back side of the semiconductor substrate 9.

[0063] The cleaning step is conducted in the following way. A mixture of  $\text{C}_2\text{F}_6$  with 300 sccm and oxygen with 700 sccm is introduced as a cleaning gas to the inside of the reaction chamber 2 from the showerhead 4. With the pressure in the reaction chamber 2 within a range of 2-5 Torr, 13.56 MHz of radiofrequency energy of 500 w-2,000 w is applied to the showerhead 4 to cause a plasma discharge region between the showerhead 4 and the ceramic heater 3. The fluorine gas is activated by the plasma, which generates a fluorine-containing active species. The fluorine active species reacts with the unwanted deposits adhering to the inside of the reaction chamber 2 and eventually convert them into a gas. The gas is evacuated from the reaction chamber 2 through the aperture 20 by an evacuation pump (not shown). The temperature of the ceramic heater 3 during the cleaning steps is kept below 500° C.

[0064] Upon completion of the cleaning of the reaction chamber 2, the supply of radiofrequency energy to the showerhead 4 is stopped and the supply of  $\text{C}_2\text{F}_6$  gas to the reaction chamber 2 is stopped. The inside of the reaction chamber 2 is purged by oxygen gas. By stopping the supply of oxygen gas and instead supplying nitrogen gas, the reaction chamber 2 may be purged.

[0065] A subsequent heating step raises the temperature of the heater 3 to the film formation temperature. Nitrogen gas

is supplied to the reaction chamber 2 through the showerhead 4 at a rate of 2 liters per minute (2 slm), which holds the pressure of the reaction chamber 2 in a range of 0.5-9 Torr, and raises the temperature of the heater 3 at a rate not exceeding 20° C. per minute. Gas supplied to the reaction chamber 2 is not limited to nitrogen gas; any gas is usable as long as it does not damage parts including the heater 3 in the reaction chamber 2. The flow of gas including nitrogen gas is not limited to 2 liters per minute (2 slm); any flow may be acceptable which can keep the pressure of the reaction chamber 2.

[0066] In addition, the rate of the increase in temperature of the heater 3 is not limited to under 20° C. per minute; the temperature of the heater 3 can be raised at a rate which does not damage the heater 3. When the temperature of the heater 3 has reached the film-forming temperature, the heating step is complete. Completion of the heating step completes the automatic cleaning sequence. The next workpiece is brought in, and the thin-film forming process is conducted.

[0067] In the cooling and heating steps for changing the temperature of the heater 3, the rate of change is not limited to under 20° C. per minute. As long as the heater 3 is not damaged by the temperature change, the faster the temperature change, the shorter the automatic cleaning sequence, which enhances productivity of the thin-film forming apparatus.

#### EXAMPLE 2

[0068] Structures of Apparatus (Remote Plasma Cleaning)

[0069] FIG. 2 illustrates an example of a thin film-forming and processing apparatus 30 having a remote plasma discharge chamber, and is the same as a thin film-forming and processing apparatus of FIG. 1 except for the structure by which unwanted deposits adhering to the inside of the reaction chamber 2 are automatically removed.

[0070] In the upper portion of the reaction chamber 2 are provided a duct 5 and a valve 6 which supply reaction gas to the reaction chamber 2 for thin film-forming and processing. The reaction gas is uniformly supplied onto the surface of a workpiece 9 through a showerhead 4 having thousands of fine holes with a diameter of less than 1 mm via a duct 14 and an opening 32 of the reaction chamber 2. When conducting thin film-forming and processing of the workpiece 9, a valve 15 is closed which valve is provided on the duct 14 connecting a remote plasma discharge chamber 16 to the reaction chamber 2.

[0071] Remote Plasma Cleaning Sequence

[0072] After at least one of the thin film-forming and processing steps to the workpiece 9 in the reaction chamber 2 is complete, an automatic cleaning sequence is done which cleans unwanted deposits deposited on the inside of the reaction chamber 2. The automatic cleaning sequence is, as mentioned before, comprised of three steps of: cooling, cleaning and heating up. The cooling step supplies nitrogen gas at 2 liters per minute to the reaction chamber 2 from the duct 5 via the valve 6, junction 31, duct 14, opening 32 and showerhead 4, and lowers the temperature of the heater 3 at a rate not exceeding 20° C. per minute, keeping the pressure of the reaction chamber 2 within a range of 0.5-9 Torr.

[0073] Subsequently performed is the cleaning step which removes the unwanted deposits deposited on the inside of

the reaction chamber 2. The step is done in the following way. The supply of nitrogen gas, which is complete during the cooling down step, is suspended, and after the reaction chamber is evacuated, argon gas is injected from the duct 22 into the remote plasma discharge chamber 16 at a flow of 3 liters per minute (3 slm). At that time, with the valve 15 open and the valve 6 closed, argon gas brought in from the duct 22 is conveyed to the reaction chamber 2 through the remote plasma discharge chamber 16.

[0074] Holding the pressure of the reaction chamber 2 in a range of 0.05-8 Torr, radiofrequency discharge of 400 kHz is generated in the remote plasma discharge chamber 16. The flow of argon is gradually changed to 2 liters per minute, and NF<sub>3</sub> gas is injected from the duct 22, which is gradually raised from zero to 1 slm by a mass flow controller (not shown). The gas supplied to the remote plasma discharge chamber 16 is changed simply by gradually increasing an amount of NF<sub>3</sub>. The gas (cleaning gas) supplied to the remote plasma discharge chamber 16 in a stable state consists of 2 liters of argon per minute and 1 liter of NF<sub>3</sub> per minute. Radiofrequency discharge plasma generated in the remote plasma discharge chamber 16 produces a fluorine active species. The cleaning gas including the fluorine active species is injected to the showerhead 4 from the upper opening 32 of the reaction chamber 2 through the valve 15 and duct 14. The cleaning gas, which is introduced into the reaction chamber 2 through thousands of small holes provided on the shower head 4, transforms into gas the unwanted deposits deposited on the inside of the reaction chamber 2 and evacuates them from the reaction chamber 2. During the cleaning step, the temperature of the heater 3 should be held at least below 500° C.

[0075] The flow rate of the cleaning gas injected into the remote plasma discharge chamber 16 during the cleaning step is not limited to the previously described flow rate, and may be selected from the range of 100 sccm to 5 slm regarding NF<sub>3</sub> and from the range of 100 sccm to 5 slm regarding argon. As cleaning gas, instead of argon gas, rare gas such as helium may be used. Instead of NF<sub>3</sub>, CF<sub>4</sub> gas such as C<sub>2</sub>F<sub>6</sub> may be used. At that time, in addition to, or instead of, argon gas, oxygen gas can be mixed.

[0076] During the cleaning step, the temperature of the heater is kept below 500° C., preferably below 470° C., and more preferably below 450° C. Power frequency supplied to the remote plasma discharge chamber 16 is not limited to 400 kHz, and may be selected from 300-500 kHz. The value of the power must be one by which a predetermined fluorine active species can be obtained. In the embodiment of the invention, power of 2,000-5,000 W at 400 kHz is used to generate radiofrequency discharge plasma in the remote plasma discharge chamber 16.

[0077] After the unwanted deposits adhering to the inside of the reaction chamber 2 are completely removed from the inside of the reaction chamber 2 by the cleaning gas with the fluorine active species, the supply of NF<sub>3</sub> gas injected from the duct 22 is suspended and the radiofrequency discharge in the remote plasma discharge chamber 16 is stopped. Even after the suspension of the supply of NF<sub>3</sub> gas and the radiofrequency discharge, argon gas is furnished to the reaction chamber 2 from the duct 22 via the remote plasma discharge chamber 16, which purges the cleaning gas with the fluorine active species remaining in the reaction chamber

2. The heating step begins, which commences purging in the reaction chamber 2 by argon gas and raises the temperature of the heater 3 to the film-forming temperature. The heat-up step is executed the same way as the aforementioned cooling step except for raising the temperature of the heater 3 at a speed of less than 20° C. per minute. When the temperature of the heater 3 reaches the temperature (the film-forming temperature) at which thin film-forming and processing of the workpiece 9 is conducted, the heating step is complete.

[0078] While cooling and heating are being conducted, introduction of nitrogen gas into the reaction chamber 2 may also be performed in the following alternative way. A predetermined flow of nitrogen gas is furnished to the duct 22 and injected to the reaction chamber 2 via the remote plasma discharge chamber 16, valve 15, and duct 14. At this time, the valve 6 is closed and plasma discharge in the remote plasma discharge chamber 16 is not performed. Via the remote plasma discharge chamber 16 from the duct 22, injection of argon gas into the reaction chamber 2, and the cooling and heating steps can also be executed.

#### [0079] Cleaning Results

[0080] Embodiments in accordance with the invention will be explained. The result when a silicon nitride film was formed on the semiconductor at the film-forming temperature 600° C. will be described below. The apparatus used was the thin film-forming and processing apparatus 30 in FIG. 2. The first semiconductor substrate 9, the workpiece, comprising aluminum nitride substrate, was placed on the ceramic heater 3. The ceramic heater 3 was held at 600° C. because of the resistance heater 26 embedded, which heated the first semiconductor substrate 9 supported on the ceramic heater 3 to 550° C. from approximately 540° C.  $\text{SiH}_4$  gas and nitrogen were mixed and introduced from the duct 5. The mixed gas was uniformly distributed, by the showerhead 4, on the surface of the first semiconductor substrate 9 placed on the heater 3 in the reaction chamber 2.

[0081] 400 W radiofrequency energy of 13.56 MHz were applied to the showerhead 4, and a plasma region was formed between the showerhead 4 and the heater supporting the first semiconductor substrate 9. A silicon nitride film of 100 nm was then formed on the surface of the first semiconductor substrate 9. After opening the gate 18 and removing the first semiconductor substrate 9, on which a silicon nitride film was formed, through the aperture 19 of the reaction chamber 2, a second semiconductor substrate 9 was introduced into the reaction chamber 2 by the same route as above and was placed on the heater 3 to form a silicon nitride film.

[0082] As with the previous film-formation and processing of the silicon nitride film, the silicon nitride film is formed on the second semiconductor substrate 9. In this way, the film-formation and processing of the silicon nitride film was consecutively performed on 25 substrates. After the 25th substrate that had completed the film-formation and processing was removed from the reaction chamber 2, the automatic cleaning sequence was executed that cleans the unwanted deposits adhering to the inside of the reaction chamber 2.

[0083] In the cooling step, the temperature of the heater 3 was lowered to 470° C. Argon gas was furnished to the remote plasma discharge chamber 16 at 3 slm from the duct

22 to set the pressure in the reaction chamber 2 at 1-1.5 Torr by opening the valve 15. After a radiofrequency discharge at 400 kHz was generated in the remote plasma discharge chamber 16, the flow of argon was gradually reduced to 2 slm, and a gradually increasing amount of  $\text{NF}_3$  gas was injected from the duct 22 till it reached 1 slm. When  $\text{NF}_3$  gas introduced from the duct 22 reached the remote plasma discharge chamber 16, a fluorine active species was generated. The fluorine active species generated in the remote plasma discharge chamber 16 was, with other gas, introduced into the reaction chamber 2 from the showerhead 4 via the valve 15, duct 14 and aperture 32. The unwanted deposits adhering to the inside of the reaction chamber 2 were cleaned by the fluorine active species.

[0084] The cleaning step by the fluorine active species corresponded to the aforementioned cleaning step, and it lasted approximately 70 seconds. After the cleaning of the reaction chamber 2 was complete, radiofrequency discharge in the remote plasma discharge chamber 16 and the supply of  $\text{NF}_3$  were both suspended. The supply of argon gas from the duct 22 was then stopped, the valve 15 was closed, and nitrogen gas was provided from the duct 5. Upon this step, the heating step was conducted, raising the temperature up to 600° C.

[0085] Conducting the silicon nitride film formation and processing in sets of 25 consecutive semiconductor substrates and then conducting the automatic cleaning sequence once, the silicon nitride film formation and processing of 2,000 semiconductor substrates was conducted.

[0086] FIG. 3 illustrates the measurement results of the thickness of formed silicon nitride films (reproducibility of film thickness). Dispersion of the thickness of grown silicon nitride films (reproducibility of film thickness) is  $\pm 1.1\%$  ( $1\sigma=0.92\%$ ), which is a good result.

[0087] FIG. 4 illustrates the distribution lines of the thickness of formed silicon nitride films on one semiconductor substrate 9 (uniformity of film thickness). The distribution lines of the thickness are  $\pm 2.0\%$  on the average for the 2,000 consecutively formed films, which are good and stable.

[0088] FIG. 5 illustrates the measurement results of particles on the surface of semiconductor substrates after the formation of silicon nitride films. The highest detected number of particles is 9 and the average value per semiconductor substrate is 3.3, which shows that the surface of semiconductor substrates is very clean.

#### [0089] Other Aspects and Effects

[0090] The present invention is directed to an automatic cleaning method and apparatus therefor that can clean the unwanted deposits adhering to the inside of a semiconductor substrate process apparatus, and is not limited to a film-forming method which forms films on semiconductor substrates. According to the plasma CVD method, an explanation is made based on the formation of silicon nitride films. However, the invention is not restricted to the formation of silicon nitride films, and may be used for the formation of inorganic films of  $\text{SiO}_2$ ,  $\text{SiON}$  and  $\text{SiOF}$ ; organic films of fluorination hydrocarbon polymer, and CVD films; methylsilane, tetramethylsilane,  $\text{SiO}$ , or  $\text{SiC}$  films.

[0091] Moreover, it is clear that an automatic cleaning method in accordance with the invention may be applied to

a thermal CVD method which forms a high permittivity film such as a W type metallic thin film or  $Ta_2O_5$ , and may effectively be used to clean the inside of the thin film-forming and processing apparatus.

[0092] When cleaning unwanted deposits adhering to the inside of the reaction chamber, since the surface temperature of the heater supporting the semiconductor substrate is, in an embodiment, lowered below  $500^\circ\text{C}$ , the adherence of aluminum fluoride to the shower head surface can be prevented. Since there is no adherence of aluminum fluoride to the showerhead surface, thin-film forming and processing of the semiconductor substrate can be performed with constant quality of the films formed.

[0093] Since aluminum fluoride is not accreted to the shower head surface in an embodiment, particles are not generated from the accreted aluminum fluoride, and the semiconductor substrate can be free of contaminants. Since the unwanted deposits adhering to the inside of the reaction chamber can be removed by automatic cleaning sequence, no particle contamination may be generated on the semiconductor. In addition, since aluminum fluoride is not generated, in-operation time of the cleaning apparatus can be reduced, which can provide a thin-film formation apparatus with high productivity.

[0094] It will be understood by those of skill in the art that numerous and various modifications can be made without departing from the spirit of the present invention. Therefore, it should be clearly understood that the forms of the present invention are illustrative only and are not intended to limit the scope of the present invention.

What is claimed is:

1. A method of continuously depositing films on substrates, comprising:

- (i) depositing a film on a substrate placed on an aluminum nitride susceptor provided in a reaction chamber by CVD using a gas introduced into the reaction chamber through a showerhead provided in the reaction chamber, said susceptor having a temperature of  $500\text{--}650^\circ\text{C}$ ;
- (ii) repeating step (i) pre-selected times;
- (iii) reducing the temperature of the susceptor to  $470^\circ\text{C}$  or lower for cleaning;
- (iv) contacting the inside of the reaction chamber including the showerhead with fluorine radicals at a pressure of  $0.5\text{--}9$  Torr, said showerhead having a temperature of  $100\text{--}250^\circ\text{C}$  which is lower than the temperature of the susceptor;
- (v) cleaning the unwanted deposits by the fluorine radicals, wherein gaseous aluminum fluoride is inhibited from being emitted from the susceptor and solidified on the showerhead by maintaining the temperature of the susceptor at  $470^\circ\text{C}$  or lower;
- (vi) upon completion of the cleaning, raising the temperature of the susceptor to  $500\text{--}650^\circ\text{C}$  for film formation; and
- (vii) repeating steps (i) through (vi) at least 40 times without interruption.

2. The method according to claim 1, wherein the cleaning is conducted at a temperature of the susceptor of  $450^\circ\text{C}$  or less.

3. The method according to claim 1, wherein the fluorine radicals are produced in a plasma discharge region generated in the reaction chamber.

4. The method according to claim 1, wherein the fluorine radicals are produced in a remote plasma discharge chamber prior to introduction of the cleaning gas into the reaction chamber, said remote plasma discharge chamber being disposed separately from the reaction chamber.

5. The method according to claim 1, wherein the unwanted deposits include at least one of silicon nitride, silicon oxide, SiOF, SiC, SiON, or hydrocarbon.

6. The method according to claim 1, wherein the reaction chamber is for plasma CVD or thermal CVD.

7. The method according to claim 1, wherein steps (iii) and (vi) further comprise introducing an inert gas into the reaction chamber while reducing and raising the temperature of the susceptor.

8. The method according to claim 1, wherein the temperature of the susceptor is changed at a rate of  $20^\circ\text{C}$  or less per minute in steps (iii) and (vi).

9. The method according to claim 1, wherein step (vii) is conducted without raising a non-uniformity of thickness of a film formed in step (a) to more than 3%.

10. The method according to claim 1, wherein step (vii) is conducted at least 80 times without raising a non-uniformity of thickness of a film formed in step (a) to more than 3%.

11. A method for preventing aluminum fluoride from depositing on a showerhead during cleaning of a reaction chamber, comprising:

- (a) after forming by CVD a film on a substrate on an aluminum nitride susceptor having a temperature of  $500\text{--}650^\circ\text{C}$ , reducing the temperature of the susceptor to  $470^\circ\text{C}$  or lower for cleaning;
  - (b) contacting the inside of the reaction chamber including the showerhead with fluorine radicals at a pressure of  $0.5\text{--}9$  Torr, said showerhead having a temperature of  $100\text{--}250^\circ\text{C}$  which is lower than the temperature of the susceptor;
  - (c) cleaning unwanted deposits inside the reaction chamber by the fluorine radicals while inhibiting generation and emission of gaseous aluminum fluoride from the susceptor and solidification of the aluminum fluoride on the showerhead by maintaining the temperature of the susceptor at  $470^\circ\text{C}$  or lower; and
  - (d) upon completion of the cleaning, raising the temperature of the susceptor to  $500\text{--}650^\circ\text{C}$  for film formation.
12. The method according to claim 11, wherein the cleaning is conducted at a temperature of the susceptor of  $450^\circ\text{C}$  or less.
13. The method according to claim 11, wherein the fluorine radicals are produced in a plasma discharge region generated in the reaction chamber.
14. The method according to claim 11, wherein the fluorine radicals are produced in a remote plasma discharge chamber prior to introduction of the cleaning gas into the reaction chamber, said remote plasma discharge chamber being disposed separately from the reaction chamber.

15. The method according to claim 11, wherein the unwanted deposits include at least one of silicon nitride, silicon oxide, SiOF, SiC, SiON, or hydrocarbon.

16. The method according to claim 11, wherein the reaction chamber is for plasma CVD or thermal CVD.

17. The method according to claim 11, wherein steps (a) and (d) further comprise introducing an inert gas into the reaction chamber while reducing and raising the temperature of the susceptor.

18. The method according to claim 11, wherein the temperature of the susceptor is changed at a rate of 20° C. or less per minute in steps (a) and (d).

19. The method according to claim 11, wherein steps (a) though (d) are repeated without interruption at least 40 times without raising a non-uniformity of thickness of a film formed in step (a) to more than 3%.

20. The method according to claim 11, wherein steps (a) though (d) are repeated without interruption at least 80 times without raising a non-uniformity of thickness of a film formed in step (a) to more than 3%.

21. The method according to claim 11, wherein the susceptor temperature is 550-600° C. in steps (a) and (d).

\* \* \* \* \*

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 697 467 A1

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
21.02.1996 Bulletin 1996/08

(51) Int Cl<sup>6</sup>: C23C 16/44, H01J 37/32

(21) Application number: 95304784.2

(22) Date of filing: 10.07.1995

(84) Designated Contracting States:  
AT BE CH DE DK ES FR GB GR IE IT LI LU NL SE

(30) Priority: 21.07.1994 US 278605

(71) Applicant: APPLIED MATERIALS, INC.  
Santa Clara, California 95054-3299 (US)

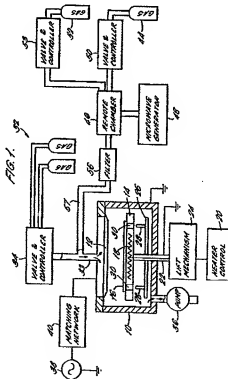
(72) Inventors:

- Shang, Guanyuan  
San Jose, California 95129 (US)
- Law, Kam S.  
Union City, California 94587 (US)
- Maydan, Dan  
Los Altos Hills, California 94022 (US)

(74) Representative: Baylles, Geoffrey Cyril et al  
London EC4A 1PQ (GB)

## (54) Method and apparatus for cleaning a deposition chamber

(57) A method for cleaning a deposition chamber (10) that is used in fabricating electronic devices including the steps of delivering a precursor gas into a remote chamber (46) that is outside the deposition chamber, activating the precursor gas in the remote chamber using a microwave generator (45) to form a reactive species, flowing the reactive species from the remote chamber into the deposition chamber via conduit (57), and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.



## APPENDIX B

Appl. No.: 10/759,953

EP 0 697 467 A1

## Description

Plasma assisted chemical reactions have been widely used in the semiconductor and flat panel display industries. One example is plasma-enhanced chemical vapor deposition (PECVD), which is a process that is used in the manufacture of thin film transistors (TFT) for active-matrix liquid crystal displays (AMLCDs). In accordance with PECVD, a substrate is placed in a vacuum deposition chamber that is equipped with a pair of parallel plate electrodes. One of the electrodes, e.g. the lower electrode, generally referred to as a susceptor, holds the substrate. The other electrode, i.e., the upper electrode, functions as a gas inlet manifold or shower head. During deposition, a reactant gas flow into the chamber through the upper electrode and a radio frequency (RF) voltage is applied between the electrodes to produce a plasma within the reactant gas. The plasma causes the reactant gas to decompose and deposit a layer of material onto the surface of the substrate.

Though such systems are designed to preferentially deposit the material onto the surface of the substrate, they also deposit some material onto other interior surfaces within the chamber. Consequently, after repeated use, these systems must be cleaned to remove the deposited layer of material that has built up in the chamber. To clean the chamber and the exposed components within the chamber, an in-situ dry cleaning process is commonly used. According to the in-situ technique, precursor gases are supplied to the chamber. Then, by locally applying a glow discharge plasma to the precursor gases within the chamber, reactive species are generated. The reactive species clean the chamber surfaces by forming volatile compounds with the process deposit on those surfaces.

This in-situ cleaning technique has several disadvantages. First, it is inefficient to use a plasma within the chamber to generate the reactive species. Thus, it is necessary to use relatively high powers to achieve an acceptable cleaning rate. The high power levels, however, tend to produce damage to the hardware inside of the chamber thereby significantly shortening its useful life. Since the replacement of the damaged hardware can be quite costly, this can significantly increase up the per substrate cost of product that is processed using the deposition system. In the current, highly competitive semiconductor fabrication industry where per substrate costs are critical to the cost conscious purchasers, the increased operating costs resulting from having to periodically replace parts that are damaged during the cleaning process is very undesirable.

Another problem with the conventional in-situ dry cleaning processes is that the high power levels that are required to achieve acceptable cleaning rates also tend to generate residues or byproducts that can damage other system components or which cannot be removed except by physically wiping off the internal surfaces of the chamber. For example, in a  $\text{Si}_3\text{N}_4$  deposition system

which uses  $\text{NF}_3$  for cleaning,  $\text{N}_2\text{H}_2\text{F}_2$  compounds tend to be generated. These ammonium compounds deposit in the vacuum pump where they can negatively affect the reliability of the pump. As another example, in a deposition system in which the chamber or the process kit components (e.g. heater, shower head, clamping rings, etc.) are made of aluminum, an  $\text{NF}_3$  plasma is often used to clean the interior surfaces. During the cleaning process, a certain amount of  $\text{AlF}_3$  is formed. The amount that is formed is greatly increased by the ion bombardment that results from the high plasma energy levels. Thus, a considerable amount of  $\text{AlF}_3$  can be formed in the system. Unfortunately, this material cannot be etched away by any known chemical process, so it must be removed by physically wiping the surfaces.

In accordance with the present invention, a remote excitation source is used outside of the process chamber to generate a reactive species which is then supplied to the process chamber to assist in carrying out a particular process, e.g. dry cleaning the chamber. In the case of the dry cleaning process, the remote excitation source breaks down the feed gas (e.g. a compound of chlorine or fluorine) to form a long lived halogen species. A second local excitation source may then optionally be used inside the chamber to sustain the long lived species and/or to further break down the gas to form the reactive species. Since the remote excitation source is relied upon to generate the reactive species, the local excitation source may be operated at much lower power levels than are required in a conventional systems. Thus, by moving the excitation source outside of the chamber, high plasma power levels are no longer needed inside the chamber to achieve acceptable cleaning rates. Indeed, in some cases it may not even be necessary to use any local excitation source (e.g. plasma) within the chamber.

In general, in one aspect, the invention is a method for cleaning a deposition chamber that is used in fabricating electronic devices. The method includes the following steps: delivering a precursor gas into a remote chamber that is separate from the deposition chamber; activating the precursor gas in the remote chamber to form a reactive species; flowing the reactive species from the remote chamber into the deposition chamber; and using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.

In general, in another aspect, the invention is a method of performing a process to fabricate electronic devices within a process chamber. The method includes the steps of: delivering a precursor gas into a remote chamber that is separate from the process chamber; activating the precursor gas in the remote chamber to form a reactive species; flowing the reactive species from the remote chamber into the process chamber; using a local activation source to further excite the reactive species that has been flowed into the process chamber from the remote chamber; and using the reactive species that has



been further excited by the local activation source in performing the fabrication process in the process chamber.

In general, in yet another aspect, the invention is a deposition apparatus that can be connected to a source of precursor gas for cleaning. The apparatus includes a deposition chamber, a first activation source adapted to deliver energy into the deposition chamber, a remote chamber that is separate from the deposition chamber, a second activation source separate from the first activation source and adapted to deliver energy into the remote chamber, a first conduit for flowing a precursor gas from a remote gas supply into the remote chamber where it is activated by the second activation source to form a reactive species, and a second conduit for flowing the reactive species from the remote chamber into the deposition chamber.

Technically, the remote plasma is used to generate reactive species. To help solve the problem of quenching of the reactive species while its flowing to the chamber a mild plasma may be applied in the process chamber to assist the cleaning. The use of the combined plasma sources achieves a better cleaning rate than would be associated with using either a local or a remote plasma alone. In addition, because of the invention permits the use of a low energy plasma (or even no plasma) within the deposition chamber, much less damage is done to the internal chamber components as a result of the cleaning process and there is much less formation of particulates and undesirable byproducts, such as  $Al_2F_6$ , the disadvantages of which were described above. In addition, in embodiments which use both remote and local excitation sources, each source can be independently adjusted to achieve optimum results. Moreover, in the case that a local plasma is not available in the system, some other activation techniques may be applied (such as thermal excitation).

A further advantage of the invention is that unwanted byproducts that are formed when activating the reactive species can easily be filtered out before the reactive species enters the deposition chamber. In addition, use of the local source to sustain the activated species lessens the restrictions that might exist on the placement of the remote activation chamber. That is, the remote activation chamber can be placed conveniently, even at further distances from the deposition chamber, with less concern about quenching of the activated species as it is being transferred from the remote chamber to the deposition chamber. This means that it will be relatively easy to retrofit existing systems with this capability.

Using the combination of remote and local excitation sources has the further advantage that it can be applied to a wide variety of applications and systems with similar benefits. For example, it can also be used in PVD and CVD systems, plasma etching systems, and systems for cleaning substrates, ion doping, and stripping of photoresist.

Other advantages and features will become apparent from the following description of the preferred em-

bodiment and from the claims.

Fig. 1 shows a block diagram of a PECVD system which embodies the invention.

In the described embodiment, we used a model AKT-1600 PECVD System manufactured by Applied Katsush Technology, modified as described herein. The AKT-1600 PECVD is designed for use in the production of active-matrix liquid crystal displays (AMLCDs). It is a modular system with multiple process chambers which can be used for depositing amorphous silicon, silicon nitride, silicon oxide and oxynitride films. The invention, however, may be used with any commercially available deposition system.

Referring to Fig. 1, the PECVD system modified in accordance with invention includes a deposition chamber 10 inside of which is a gas inlet manifold (or shower head) 12 for introducing deposition gases and a susceptor 14 for holding a substrate 16 onto which material is to be deposited. The inlet manifold 12 and the susceptor 14, which are both in the form of parallel plates, also function as upper and lower electrodes, respectively. The lower electrode and the chamber body are connected to ground. An RF generator 38 supplies RF power to the upper electrode through a matching network 40. The RF generator 38 is used to generate a plasma between the upper and lower electrodes.

The susceptor 14 includes a resistive heater 18 for heating the substrate during deposition. An external heater control module 20 powers the heaters to achieve and maintain the susceptor at an appropriate temperature level as dictated by the process being run in the system.

The susceptor is attached to the top of a movable shaft 22 that extends vertically through the bottom of the chamber. A motorized lift mechanism 24 moves the shaft in a vertical direction so as to raise the susceptor into position near the inlet manifold for a deposition run and to lower the susceptor after completing the deposition run. The separation between the upper and lower electrodes is adjustable to maximize reaction kinetics and film characteristics for the particular deposition process that is being performed. Below the susceptor there is a lift-off plate 26 with a set of vertical pins 28. The pins 28 are aligned with corresponding holes 30 in the susceptor 14. When the susceptor is lowered after a processing run, the pins pass through the holes, contact the back side of the substrate, and lift the substrate off of the susceptor so that it can be more easily removed from the chamber by a mechanical transfer mechanism (not shown).

Outside of chamber 10, there is a gas supply 32 containing the gases that are used during deposition. The particular gases that are used depend upon the materials to be deposited onto the substrate. The process gases flow through an inlet port into the gas manifold and then into the chamber through the shower head. An electronically operated valve and flow control mechanism 34 controls the flow of gases from the gas supply into the

chamber. Also connected to the chamber through an outlet port is a vacuum pump 36, which is used to evacuate the chamber.

In accordance with the invention, a second gas supply system is also connected to the chamber through inlet port 33. The second gas supply system supplies gas that is used to clean the inside of the chamber after a sequence of deposition runs. By cleaning, we mean removing deposited material from the interior surfaces of the chamber.

The second gas supply system includes a source of a precursor gas 44, a remote activation chamber 46 which is located outside and at a distance from the deposition chamber, a power source 48 for activating the precursor gas within the remote activation chamber, an electronically operated valve and flow control mechanism 50, and a stainless steel conduit or pipe 57 connecting the remote chamber to the deposition chamber. The valve and flow control mechanism 50 delivers gas from the source of precursor gas 44 into the remote activation chamber 46 at a user-selected flow rate. The power source 48 activates the precursor gas to form a reactive species which is then flowed through the conduit 57 into the deposition chamber via inlet port 33. In other words, the upper electrode or shower head 12 is used to deliver the reactive gas into the deposition chamber. In the described embodiment, the remote chamber is a quartz tube and the power source is a 2.54 GHz microwave generator with its output aimed at the quartz tube.

Optionally, there may also be a source of a minor carrier gas 52 that is connected to the remote activation chamber through another valve and flow control mechanism 53. The minor carrier gas aids in the transport of the activated species to the deposition chamber. It can be any appropriate nonreactive gas that is compatible with the particular cleaning process with which it is being used. For example, the minor carrier gas may be argon, nitrogen, helium, hydrogen, or oxygen, etc. In addition to aiding in the transport of activated species to the deposition chamber, the carrier gas may also assist in the cleaning process or help initiate and/or stabilize the plasma in the deposition chamber.

In the described embodiment, there is a filter 56 in the conduit or pipe through which the activated species passes before entering the deposition chamber. The filter removes particulate matter that might have been formed during the activation of the reactive species. In the described embodiment, the filter is a made of ceramic material having a pore size of about 0.01 to 0.03 microns. Of course, other materials can also be used, for example, teflon.

It should be noted that the filter can also be used to remove unwanted materials that might have been produced as byproducts of the reaction within the remote chamber. For example, if the reactive gas is  $CF_4$  or  $SF_6$  or some other halogen compound containing either carbon or sulfur, an activated carbon or sulfur species will be present as a byproduct of the activation process. It is

generally desired, however, that carbon and sulfur not be present in the deposition chamber. This is why these compounds are generally not used in conventional dry cleaning process where the activation occurs entirely within the deposition chamber. However, when the activation is performed remotely, as described herein, these materials can be easily removed by using an appropriate filter material. Such filter materials are readily available in the commercial market and are well known to persons of ordinary skill in the art.

In the described embodiment, the precursor is  $NF_3$ . The flow rate of activated species is about 2 liters per minute and the chamber pressure is about 0.5 Torr. To activate the precursor gas, the microwave source delivers about 500-1500 Watts to the activation chamber. Within the deposition chamber, the RF source supplies about 100-200 Watts to the plasma. For the AKT-1600 PECVD system this implies a voltage between the upper and lower electrodes of about 15-20 volts. Of course, the precise voltage and current are pressure dependent, i.e., the current is proportional to the pressure given a fixed voltage. In any event, it is only necessary to induce a gentle plasma within the chamber, which only need be strong enough to sustain the activated species that has been flowed into the chamber from the remote source.

By using  $NF_3$  as the feed gas, we have been able to clean chambers that have been deposited with silicon (Si), doped silicon, silicon nitride ( $Si_3N_4$ ) and silicon oxide ( $SiO_2$ ). The cleaning rate for as-deposited film has reached 2 micron/minute for silicon nitride and 1 micron/minute for silicon, doped silicon, and silicon oxide. These cleaning rates are two to four times faster than the conventional cleaning process which employs only a local plasma with a power level of about 2 kilowatts at 13.56 MHz RF.

Though a microwave generator was used in the described embodiment to activate the precursor gas, any power source that is capable of activating the precursor gas can be used. For example, both the remote and local plasmas can employ DC, radio frequency (RF), and microwave (MW) based discharge techniques. In addition, if an RF power source is used, it can be either capacitively or inductively coupled to the inside of the chamber. The activation can also be performed by a thermally based, gas break-down technique; a high intensity light source; or an X-ray source, to name just a few.

In general, the reactive gases may be selected from a wide range of options, including the commonly used halogens and halogen compounds. For example, the reactive gas may be chlorine, fluorine or compounds thereof, e.g.,  $NF_3$ ,  $CF_4$ ,  $SF_6$ ,  $C_2F_6$ ,  $CCl_4$ ,  $C_2Cl_6$ . Of course, the particular gas that is used depends on the deposited material which is being removed. For example, in a tungsten deposition system a fluorine compound gas is typically used to etch and/or remove clean the deposited tungsten.

Because of the use of a local plasma in conjunction with the remote plasma, the remote activation chamber

can be placed farther away from the chamber. Thus, only tubing is needed to connect the two remote sources to the local source. Some quenching of the activated species (i.e., deactivation of the activated species) may occur during the transfer. However, the local source compensates for any such quenching that may occur. In fact, some long lived activated species (e.g.  $F^*$ ) typically do not return to the ground state when quenched but rather they transition to an intermediate state. Thus, the amount of energy that is required to reactivate the quenched species is much less than is required to activate the gas in the remote activation chamber. Consequently, the local activation source (e.g. plasma) need not be a high energy source.

It should also be noted that by placing the remote source at a distance from the deposition chamber, the short lived radicals that are produced during the activation process will be quenched more completely than the long lived radicals as both are transferred to the deposition chamber. Thus, the reactive gas that flows into the deposition chamber will contain primarily the long lived radicals that have survived the transfer. For example, if  $NF_3$  is the reactive gas, two radicals are produced in the remote activation chamber, namely,  $N^*$  and  $F^*$ . The nitrogen radical is short lived and the fluorine radical is long lived. The nitrogen radical will typically not survive a long transfer from the remote chamber to the deposition chamber, whereas, a large percentage of the fluorine radicals will survive. This is a form of natural filtering that occurs in the system that may be very desirable. In the case of nitrogen radicals, for example, it is sometimes preferable that they not be present in the deposition chamber because their presence may result in the formation of  $N_xH_yF_z$  compounds, which, as previously described, can harm the pump. When the activation is performed in the deposition chamber, however, as in the case of conventional cleaning techniques, there is no easy way to eliminate the nitrogen radicals that are produced.

In the dry cleaning process, chamber pressure can be selected to lie anywhere within a fairly broad range of values without significantly affecting performance. The preferred pressure range is from about 0.1 to about 2 Torr, although pressures outside of that range can also be used. In addition, the frequencies that were chosen for the described embodiment were merely illustrative and the frequencies that may be used in the invention are not restricted to those used in the described embodiment. For example, with regard to the RF power source, any of a wide range of frequencies (e.g. 400 kHz to 13.56 MHz) are typically used to generate plasmas and those frequencies may also be used in the invention. In general, however, it should be understood that the power levels, flow rates, and pressures that are chosen are system specific and thus they will need to be optimized for the particular system in which the process is being run. Making the appropriate adjustments in process conditions to achieve optimum of performance for a particular system

is well within the capabilities of a person of ordinary skill in the art.

Although the described embodiment involved a PECVD system, the invention has far wider applicability. For example, the concept of a remote activation source (i.e., outside the main vacuum chamber), possibly used in conjunction with a local activation source (i.e., inside the main vacuum chamber) can be used in systems designed for any of the following purposes: PVD, CVD, ion doping, photoresist stripping, substrate cleaning, plasma etching.

Other embodiments are within the following claims.

# 15 Claims

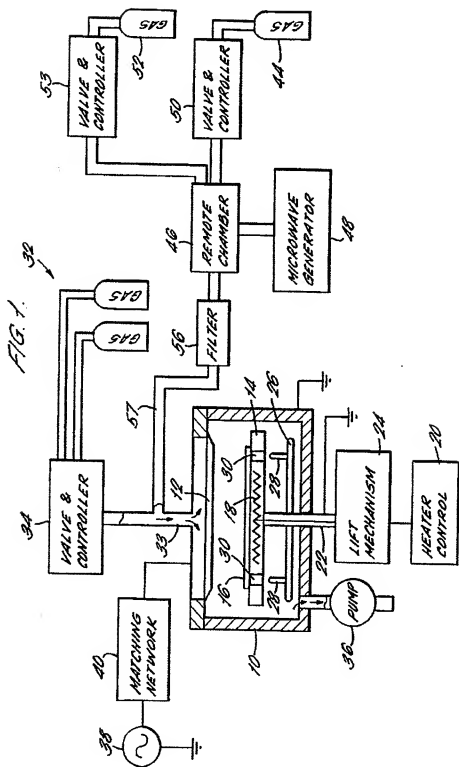
1. A method for cleaning a deposition chamber that is used in fabricating electronic devices, said method comprising:
  - 20 delivering a precursor gas into a remote chamber that is outside of the deposition chamber;
  - activating the precursor gas in the remote chamber to form a reactive species;
  - 25 flowing the reactive species from the remote chamber into the deposition chamber; and
  - using the reactive species that is flowed into the deposition chamber from the remote chamber to clean the inside of the deposition chamber.
- 30 2. The method of claim 1 wherein the step of activating the precursor gas is performed by using a remote energy source.
- 35 3. The method of claim 1 further comprising using a local energy source to further excite the reactive species that has been flowed into the deposition chamber from the remote chamber.
- 40 4. The method of claim 3 wherein the precursor gas is selected from the group of gases consisting of all halogens and gaseous compounds thereof.
- 45 5. The method of claim 4 wherein the precursor gas is selected from the group of gases consisting of chlorine, fluorine, and gaseous compounds thereof.
- 50 6. The method of claim 2 wherein the remote energy source is a microwave energy source.
- 55 7. The method of claim 6 wherein the precursor gas is selected from the group of gases consisting of all halogens and gaseous compounds thereof.
8. The method of claim 7 wherein the precursor gas is selected from the group of gases consisting of chlorine, fluorine, and compounds thereof.
9. The method of claim 2 wherein the local energy

source is an RF energy source for generating a plasma within the deposition chamber.

10. The method of claim 2 further comprising filtering the reactive species before it enters the deposition chamber to remove unwanted materials. 5
11. The method of claim 2 further comprising flowing a carrier gas into the remote activation chamber. 10
12. The method of claim 11 wherein the carrier gas is selected from the group of gases consisting of nitrogen, argon, helium, hydrogen, and oxygen. 15
13. A method of performing a process to fabricate electronic devices within a process chamber, said method comprising:  
delivering a precursor gas into a remote chamber that is outside of the process chamber;  
activating the precursor gas in the remote chamber and to thereby form a reactive species;  
flowing the reactive species from the remote chamber into the process chamber;  
using a local activation source to further excite the reactive species that has been flowed into the process chamber from the remote chamber; and  
using the reactive species that has been further excited by the local activation source in performing the fabrication process in the process chamber. 20
14. The method of claim 13 wherein the step of activating the precursor gas is performed by using a remote energy source. 25
15. The method of claim 13 wherein the precursor gas is selected from a group of gases consisting of halogen gases and compounds thereof. 30
16. The method of claim 15 wherein the precursor gas is selected from a group of gases consisting of chlorine, fluorine, and compounds thereof. 35
17. The method of claim 14 wherein the remote energy source is a microwave energy source. 40
18. The method of claim 17 wherein the precursor gas is selected from a group of gases consisting of halogen gases and compounds thereof. 45
19. The method of claim 18 wherein the precursor gas is selected from a group of gases consisting of chlorine, fluorine, and compounds thereof. 50
20. The method of claim 13 wherein the local energy source is an RF energy source for generating a plasma within the process chamber. 55
21. The method of claim 13 further comprising filtering

the reactive species before it enters the deposition chamber to remove unwanted materials.

22. The method of claim 13 further comprising flowing a carrier gas into the remote activation chamber. 5
23. The method of claim 22 wherein the carrier gas is selected from a group of gases consisting of nitrogen, argon, helium, hydrogen, and oxygen. 10
24. A deposition apparatus that can be connected to a source of precursor gas for cleaning, said apparatus comprising:  
a deposition chamber;  
a first activation source adapted to deliver energy into said deposition chamber;  
a remote chamber that is outside of said deposition chamber;  
a second activation source separate from said first activation source and adapted to deliver energy into said remote chamber;  
a first conduit for flowing a precursor gas from a remote gas supply into the remote chamber where it is activated by said second activation source to form a reactive species; and  
a second conduit for flowing the reactive species from the remote chamber into the deposition chamber. 15
25. The apparatus of claim 24 further comprising a valve and flow control mechanism which controls the flow of precursor gas into the remote chamber. 20
26. The apparatus of claim 25 further comprising a valve and flow control mechanism which controls the flow of a carrier gas that is different from the precursor gas into the remote chamber. 25
27. The deposition apparatus of claim 25 further comprising a filter in the second conduit to remove unwanted materials out of the flow of reactive species from the remote chamber. 30



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 95 30 4784

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL4)
X	US-A-5 328 558 (KAWAMURA KOUHEI) 12 July 1994	13-20, 22-26 21,27	C23C16/44 H01J37/32
Y	* column 3, line 18 - column 4, line 2; claim 1 *		
A	* column 5, line 58 - column 6, line 68 *	1-9,11, 12	
	-----		
X	DE-A-41 32 559 (SIEMENS AG) 8 April 1993	1-9,11, 12,24-26 10,27 13-23	C23C
Y	* claims 1,2 *		
A	-----		
Y	PROCEEDINGS OF THE FIRST INTERNATIONAL SYMPOSIUM ON ULTRA LARGE INTEGRATION SCIENCE AND TECHNOLOGY: ULSI SCIENCE AND TECHNOLOGY/1987, PHILADELPHIA, PA, USA, 11-15 MAY 1987, 1987, PENNINGTON, NJ, USA, ELECTROCHEM. SOC, USA, pages 805-821, OHMI T ET AL 'Ultra clean gas delivery system for ULSI fabrication and its evaluation' * page 808, line 1 - line 16 *	10,21,27	
X	EP-A-0 555 546 (IBM) 18 August 1993 * column 4, line 37 - column 5, line 1 *	1,2,6-8	C23C
X	PATENT ABSTRACTS OF JAPAN vol. 005 no. 015 (E-043), 29 January 1981 & JP-A-55 145338 (TOSHIBA CORP) 12 November 1980, * abstract *	1,2,6-8	
	-----		
X	US-A-4 867 841 (LOEWENSTEIN LEE M ET AL) 19 September 1989 * claim 1 *	13-20, 22,23	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 20 October 1995	Examiner Ekhardt, H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : number of the same patent family, corresponding document	

EPO FORM 1500 (1/93)

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant	: Satoh et al.
Appl. No.	: 10/759,953
Filed	: January 16, 2004
For	: SEMICONDUCTOR- PROCESSING DEVICE PROVIDED WITH A REMOTE PLASMA SOURCE FOR SELF- CLEANING
Examiner	: Lund, Jeffrie Robert
Group Art Unit	: 1763

DECLARATION OF KIYOSHI SATOH UNDER 37 C.F.R. § 1.132

Mail Stop AF  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Dear Sir:

I, Kiyoshi Satoh, do hereby declare and say as follows:

1. I am currently employed as a manager of a technical support group in the department of Customer Service at ASM Japan K.K. I joined ASM Japan K.K. in 1991 as a member of the Research and Development group. Over the last 16 years, I have worked in various capacities as a research and development engineer, project manager, and most recently as a manager of the technical support group in the customer service department. In particular, my work has focused on the development of plasma CVD deposition processes and apparatus. I am an inventor on various patents in the field of semiconductor fabrication, including the following U.S. patents: 6,193,803, 6,120,605, 6,767,836, 6,235,112, 6,113,704, 6,435,798, 6,736,147, 6,761,771, 6,919,270, 6,991,959, and 6,815,332. I am also listed as an inventor on the present patent Application. Prior to my work in the semiconductor industry, I earned a bachelor's degree in chemistry at Kumamoto University.

Appl. No. : 10/759,953  
Filed : January 16, 2004

2. I have read and understand the claims in the present patent application. I understand that the claims concern a CVD device involving a deposition reaction chamber, a plasma discharge chamber that is remote from the reaction chamber, a piping between the two, and a valve in the piping, as well as other elements. Additionally, the valve, when fully opened, allows for a pressure drop across the valve of less than about 0.25 Torr, has a valve opening that is substantially as wide as the inner surface of the piping, and/or has a valve body that does not have projections with respect to the inner surface of the piping.

3. I have read and understand the rejections in the Final Office Action dated November 16, 2006. I understand that the Examiner has asserted that U.S. Pat. Nos. 5,812,403 and 5,939,831 to Fong et al. teach a valve that, when fully opened, has an opening that is sized substantially equal in width to the inner surface of the piping and does not have projections with respect to the inner surface of the piping. In particular, the Examiner's cited support for such a teaching is allegedly found in Figures 3 and 6a of each of the Fong et al. patents.

4. After having read both U.S. Pat. Nos. 5,812,403 and 5,939,831, it is my considered opinion that these patents do not teach the relevant valve, as presently claimed and described above in paragraph 2. I understand the cited sections in Fong et al. (Figures 3 and 6a) to merely demonstrate a schematic of the concept of a gate valve and not the particularly recited valve. Figure 3 merely represents the valve as a block 280 with a fluid passage 293 passing through it. There is no disclosure of the actual valve body or how it is involved. Thus, there is no disclosure regarding the possible position of the valve body when the valve is fully opened. Figure 6a represents the valve 280 as a block with a passageway. There is no depiction of the actual valve body. Thus, while Figures 3 and 6a do depict a valve 280 in a passageway, there is no actual teaching that the valve is configured so that, when fully opened, the opening through the valve is substantially equal in width to an inner surface of the piping and/or the valve does not have projections with respect to the inner surface of the piping.

5. There is nothing in the detailed descriptions of the two Fong et al. patents that alters my above analysis of Figures 3 and 6a. Thus, the Fong et al. patents do not teach a valve with the recited characteristics of a particular maximum pressure drop or a valve body that does not have projections with respect to the inner surface of the piping.

6. It is my opinion that one of skill in the art, after reviewing the Fong et al. patents, would conclude that, in some embodiments of the disclosed device in Fong et al. a valve can be



Appl. No. : 10/759,953  
Filed : January 16, 2004

used. However, they would not conclude that Fong et al. teaches or suggests a valve with the characteristics described in paragraph 2 of this Declaration.

7. I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Respectfully submitted,

Dated: Jan. 05, 2007

By: K. Satoh

Kiyoshi Satoh

3213641  
121506